

PCT

WORLD INTELLECTUAL
PROPERTY ORGANIZATION

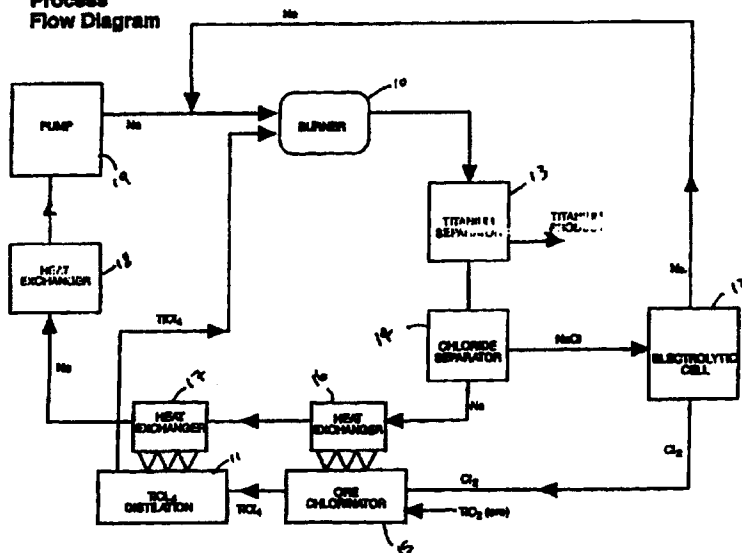


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C22C 1/00, 24/00, C22B 4/00	A1	(11) International Publication Number: WO 96/04407 (43) International Publication Date: 15 February 1996 (15.02.96)
(21) International Application Number: PCT/US95/10159 (22) International Filing Date: 25 July 1995 (25.07.95) (30) Priority Data: 08/283,358 1 August 1994 (01.08.94) US (71) Applicant: KROFTT-BRAKSTON INTERNATIONAL, INC. [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). (72) Inventors: ARMSTRONG, Donn, Reynolds; 6005 Ridge Court, Lisle, IL 60532 (US). BORYS, Stanely, S.; 300 Waxwing Avenue, Naperville, IL 60565 (US). ANDERSON, Richard, Paul; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). (74) Agent: LEVY, Harry, M.; Emrich & Dithmar, Suite 3000, 300 South Wacker Drive, Chicago, IL 60606 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, NO, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: METHOD OF MAKING METALS AND OTHER ELEMENTS

Process
Flow Diagram



(57) Abstract

A method of producing a non-metal element or a metal or an alloy thereof from a halide or mixtures thereof. The halide or mixtures thereof are contacted with a stream of liquid alkali metal or alkaline earth metal or mixtures thereof in sufficient quantity to convert the halide to the non-metal or the metal or alloy and to maintain the temperature of the reactants at a temperature lower than the lesser of the boiling point of the alkali or alkaline earth metal at atmospheric pressure or the sintering temperature of the produced non-metal or metal or alloy. A continuous method is disclosed, particularly applicable to titanium.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

Background of the Invention

This invention relates to the production of elemental material from the halides thereof and has particular applicability to those metals and non-metals for which the reduction of the halide to the element is exothermic. Particular interest exists for titanium and the present invention will be described with particular reference to titanium but is applicable to other metals and non-metals such as Al, As, Sb, Be, B, Ta, Ge, V, Nb, Mo, Ga, Ir, Os, U and Re, all of which produce significant heat upon reduction from the halide to the metal. For the purposes of this application, elemental materials include those metals and non-metals listed above or in Table 1.

At present titanium production is by reduction of titanium tetrachloride, which is made by chlorinating relatively high-grade titanium dioxide ore. Ores containing rutile can be physically concentrated to produce a satisfactory chlorination feed material; other sources of titanium dioxide, such as ilmenite, titaniferous iron ores and most other titanium source materials, require chemical beneficiation.

The reduction of titanium tetrachloride to metal has been attempted using a number of reducing agents including hydrogen, carbon, sodium, calcium, aluminum and magnesium. The magnesium reduction of titanium tetrachloride has proved to be a commercial method for producing titanium metal. However, the resultant batch process requires significant material handling with resulting opportunities for contamination and also in

quality variation from batch to batch. The greatest potential for decreasing production cost is the development of a continuous reduction process with attendant reduction in material handling.

There is a strong demand for the development of a process that enables continuous economical production of titanium powder suitable for use without additional processing for application to powder metallurgy or vacuum-arc melting to ingot form. The Kroll process and the Hunter process are the two present day methods of producing titanium commercially.

In the Kroll process, titanium tetrachloride is chemically reduced by magnesium at about 1000°C. The process is conducted in a batch fashion in a metal retort with an inert atmosphere, either helium or argon. Magnesium is charged into the vessel and heated to prepare a molten magnesium bath. Liquid titanium tetrachloride at room temperature is dispersed dropwise above the molten magnesium bath. The liquid titanium tetrachloride vaporizes in the gaseous zone above the molten magnesium bath. A surface reaction occurs to form titanium and magnesium chloride. The Hunter process is similar to the Kroll process, but uses sodium instead of magnesium to reduce the titanium tetrachloride to titanium metal and produce sodium chloride.

For both processes, the reaction is uncontrolled and sporadic and promotes the growth of dendritic titanium metal. The titanium fuses into a mass that encapsulates some of the molten magnesium (or sodium) chloride. This fused mass is

called titanium sponge. After cooling of the metal retort, the solidified titanium sponge metal is broken up, crushed, purified and then dried in a stream of hot nitrogen. Powder titanium is usually produced through grinding, shot casting or centrifugal processes. A common technique is to first cause the titanium to absorb hydrogen to make the sponge brittle to facilitate the grinding process. After formation of the powder titanium hydride, the particles are dehydrogenated to produce a usable product. The processing of the titanium sponge into a usable form is difficult, labor intensive, and increases the product cost by a factor of two to three.

During these processing steps, some sponge particles as large as several centimeters in size may be ignited in air and are thereby converted to titanium oxynitride, which is usually not destroyed during the melting operation. The resulting inclusions of hard material within the titanium metal parts have been identified as causing disastrous failures of jet engine parts, leading to crashes of aircraft.

The processes discussed above have several intrinsic problems that contribute heavily to the high cost of titanium production. Batch process production is inherently capital and labor intensive. Titanium sponge requires substantial additional processing to produce titanium in a usable form, increasing cost, increasing hazard to workers and exacerbating batch quality control difficulties. Neither process utilizes the large exothermic energy reaction, requiring substantial energy input for titanium production (approximately 6 kw-hr/kg

product metal). In addition, the processes generate significant production wastes that are of environmental concern.

Summary of the Invention

Accordingly, an object of the present invention is to provide a method and system for producing non-metals or metals or alloys thereof which is continuous having significant capital and operating costs advantages over existing batch technologies.

Another object of the present invention is to provide a method and system for producing metals and non-metals from the exothermic reduction of the halide while preventing the metal or non-metal from sintering onto the apparatus used to produce same.

Still another object of the invention is to provide a method and system for producing non-metal or metal from the halides thereof wherein the process and system recycles the reducing agent, thereby substantially reducing the environmental impact of the process.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

Brief Description of the Drawings

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a process flow diagram showing the continuous process for producing as an example titanium metal from titanium tetrachloride;

FIG. 2 is a heat balance flow sheet for a process wherein the reactants exiting the burner are about 300°C; and

FIG. 3 is an energy balance for a process in which the reactants exits the burner at about 850°C.

Detailed Description of the Invention

The process of the invention may be practiced with the use of any alkaline or alkaline earth metal depending upon the transition metal to be reduced. In some cases, combinations of an alkali or alkaline earth metals may be used. Moreover, any halide or combinations of halides may used with the present invention although in most circumstances chlorine, being the cheapest and most readily available, is preferred. Of the alkali or alkaline earth metals, by way of example, sodium will be chosen not for purposes of limitation but merely purposes of illustration, because it is cheapest and preferred, as has chlorine been chosen for the same purpose.

Regarding the non-metals or metals to be reduced, it is possible to reduce a single metal such as titanium or tantalum zirconium, selected from the list set forth hereafter. It is also possible to make alloys of a predetermined composition by providing mixed metal halides at the beginning of the process in the required molecular ratio. By way of example, Table 1 sets forth heats of reaction per gram of sodium for the reduction of non-metal or metal halides applicable to the inventive process.

Table 1

FEEDSTOCK	HEAT kJ/g
TiCl ₄	10
AlCl ₃	9
SbCl ₃	14
BeCl ₂	10
BCl ₃	12
TaCl ₅	11
VC1 ₄	12
NbCl ₅	12
MoCl ₄	14
GaCl ₃	11
UF ₆	10
ReF ₆	17

The process will be illustrated, again for purposes of illustration and not for limitation, with a single metal titanium being produced from the tetrachloride.

A summary process flowsheet is shown in Figure 1. Sodium and titanium tetrachloride are combined in a burner reaction chamber 10 where titanium tetrachloride vapor from a source thereof in the form of a distillation column 11 is injected into a flowing sodium stream from a source (not shown) thereof. Make up sodium is produced in an electrolytic cell 12. The reduction reaction is highly exothermic, forming molten reaction products of titanium and sodium chloride. The molten reaction products are quenched in the bulk sodium stream. Particle sizes and reaction rates are controlled by metering of the titanium tetrachloride vapor flowrate, dilution of the titanium tetrachloride vapor with an inert gas, such as He or Ar, and the sodium flow characteristics and mixing parameters where the burner includes concentric nozzles having an inner nozzle for the $TiCl_4$ and the outer nozzle for the liquid sodium, the gas is intimately mixed with the liquid and the resultant temperature, significantly affected by the heat of reaction, can be controlled by the quantity of sodium and maintained below the sintering temperature of the produced metal, such as titanium or about 1000°C.

The bulk sodium stream then contains the titanium and sodium chloride reaction products. These reaction products are removed from the bulk sodium stream by conventional separators 13 and 14 such as cyclones or particulate filters. Two separate options for separation of the titanium and the sodium chloride exist.

The first option removes the titanium and sodium chloride products in separate steps. This is accomplished by maintaining the bulk stream temperature such that the titanium is solid but the sodium chloride is molten through control of the ratio of titanium tetrachloride and sodium flowrates to the burner 10. For this option, the titanium is removed first, the bulk stream cooled to solidify the sodium chloride, then the sodium chloride is removed from separator 14. In this option, the process heat for titanium tetrachloride distillation would be removed from the bulk stream immediately after the titanium separator 13.

In the second option for reaction product removal, a lower ratio of titanium tetrachloride to sodium flowrate would be maintained in the burner 10 so that the bulk sodium temperature would remain below the sodium chloride solidification temperature. For this option, titanium and sodium chloride would be removed simultaneously. The sodium chloride and any residual sodium present on the particles would then be removed in a water-alcohol wash.

Following separation, the sodium chloride is then recycled to the electrolytic cell 12 to be regenerated. The sodium is returned to the bulk process stream for introduction to burner 10 and the chlorine is used in the ore chlorinator 15. It is important to note that while both electrolysis of sodium chloride and subsequent ore chlorination will be performed using technology well known in the art such integration and recycle of the reaction byproduct is not

possible with the Kroll or Hunter process because of the batch nature of those processes and the production of titanium sponge as an intermediate product. Operators of the Kroll and Hunter processes purchase titanium tetrachloride for use in the manufacture of titanium. The integration of these separate processes enabled by the inventive chemical manufacturing process has significant benefits with respect to both improved economy of operation and substantially reduced environmental impact achieved by recycle of waste streams.

Chlorine from the electrolytic cell 12 is used to chlorinate titanium ore (rutile, anatase or ilmenite) in the chlorinator 15. In the chlorination stage, the titanium ore is blended with coke and chemically converted in the presence of chlorine in a fluidized-bed or other suitable kiln chlorinator 15. The titanium dioxide contained in the raw material reacts to form titanium tetrachloride, while the oxygen forms carbon dioxide with the coke. Iron and other impurity metals present in the ore are also converted during chlorination to their corresponding chlorides. The titanium chloride is then condensed and purified by means of distillation in column 11. With current practice, the purified titanium chloride vapor would be condensed again and sold to titanium manufacturers; however, in this integrated process, the titanium tetrachloride vapor stream is used directly in the manufacturing process.

After providing process heat for the distillation step in heat exchanger 16, the temperature of the bulk process stream is adjusted to the desired temperature for the burner 10

at heat exchanger 17, and then combined with the regenerated sodium recycle stream, and injected into the burner. It should be understood that various pumps, filters, traps, monitors and the like will be added as needed by those skilled in the art.

Referring now to Figures 2 and 3, there is disclosed flow diagrams, respectively, for a low temperature process in Fig. 2 and a high temperature process in Fig. 3. The principal differences are the temperatures at which the sodium enters and leaves the burner 10. Like numbers have been applied for like equipment, the purpose of which was explained in Figure 1. For instance in Fig. 2 for the low temperature process, the sodium entering the burner 10 is at 200°C having a flow rate of 38.4 kilograms per minute. The titanium tetrachloride from the boiler 11 is at 2 atmospheres and at a temperature of 164°C, the flow rate through line 15a being 1.1 kg/min. Pressures up to 12 atmospheres may be used, but it is important that back flow be prevented, so an elevated at pressure of at least 2 atmospheres is preferred to ensure that flow through the burner nozzle is critical or choked. In all aspects, for the process of Figures 1 as well as the processes of Figures 2 and 3, it is important that the titanium that is removed from the separator 13 be at or below and preferably just below the sintering temperature of titanium in order to preclude and prevent the solidification of the titanium on the surfaces of the equipment, which is one of the fundamental difficulties with the processes commercially used presently. By maintaining the temperature of the titanium metal below the sintering

temperature of titanium metal, the titanium will not attach to the walls of the equipment as it presently does and, therefore, the physical removal of same will be obviated. This is an important aspect of this invention and is obtained by the use of sufficient Na metal or diluent gas or both to control the temperature of the elemental (or alloy) product.

By way of interest, batch processes now in use require that the titanium sponge be jackhammered from the collection vessel and considering the hardness of the sponge, is no mean task.

The high-temperature process illustrated in Fig. 3 shows that the temperature at which the sodium enters the boiler is at 750°, having a flow rate of about 33.4 kg.

The temperature of product from the burner in the low temperature process of Fig. 2 is about 300°C whereas the high temperature process is at about 850°C. It is clear that even at the high temperature process, the titanium is well below the sintering temperature which is approximately 1000°C, thereby ensuring that the shortcomings of the present day process are avoided. The heat exchangers in both Figs. 2 and 3 are identified by the numeral 20 although the values of the power removed is different for the processes of Fig. 2 (low temperature) and Fig. 3 (high temperature), due in part because of the placement of the heat exchanger 20 in the high temperature process prior to the separation of sodium chloride while in the low temperature process, the heat exchanger 20 is subsequent to the separation of sodium chloride resulting in

different power outputs as indicated. In both flow diagrams of Figs. 2 and 3, sodium make-up is indicated by the line 12A and this may come from an electrolytic cell 12 or some other source of sodium entirely different. In other aspects, both Figures 2 and 3 are illustrative of the types of design parameters which may be used to produce titanium metal in a continuous process which avoids the problems inherent in the batch process presently in use commercially.

The invention has been illustrated by reference to titanium alone and titanium tetrachloride as a feedstock, in combination with sodium as the reducing metal. However, it should be understood that the foregoing was for illustrative purposes only and the invention clearly pertains to those metals and non-metals in Table 1, which of course include the fluorides of uranium and rhenium and well as other halides such as bromides. Moreover, sodium while being the preferred reducing metal because of cost and availability, is clearly not the only available reductant. Lithium, potassium as well as calcium and other alkaline earth metals are available and thermodynamically feasible. It is well within the skill of the art to determine from the thermodynamic Tables which metals are capable of acting as a reducing agent in the foregoing reactions, the principal applications of the process being to those reactions which are highly exothermic as illustrated in Table 1 when the chloride or halide is reduced to the metal. Moreover, it is well within the skill of the art and it is contemplated in this invention that alloys can be made by the

process of the subject invention by providing a suitable halide feed in the molecular ratio of the desired alloy.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The Claims:

1. A method of producing an elemental material or an alloy thereof from a halide or mixtures thereof comprising intimately contacting the halide or mixtures thereof with a stream of liquid alkali metal or alkaline earth metal or mixtures thereof, said alkali or alkaline earth metal or mixtures thereof being present in sufficient quantity to convert the halide to elemental material or an alloy and to maintain the temperature of the reactants at a temperature lower than the lesser of the boiling point of the alkali or alkaline earth metal at atmospheric pressure or the sintering temperature of the produced elemental material or alloy to prevent the elemental material from depositing on the equipment.

2. The method of claim 1, wherein the elemental material is one or more of Ti, Al, Sb, Be, B, Ga, Mo, Nb, Ta, and V.

3. The method of claim 1, wherein the elemental material is one or more of Ir, Os, Re and U.

4. The method of claim 1, wherein the alkali metal is one or more of Na, K and Li.

5. The method of claim 1, wherein the alkaline earth metal is one or more of Ca, Sr and Ba.

6. The method of claim 1, wherein the halide is one or more of Cl, Br and F.

7. The method of claim 1, wherein the alkali metal is one or more of Na and K, the alkaline earth is one or more of Ca and Ba and the halide is one or more of Cl and Br.

8. The method of claim 1, wherein the halide is in vapor form and at a pressure in the range of from about 2 atmospheres to about 10 atmospheres when brought in contact with the liquid alkali metal or alkaline earth metal or mixtures thereof.

9. The method of claim 1, and further comprising adding a inert gas to the halide vapor as a diluent and heat sink.

10. The method of claim 9, wherein the inert gas is Ar or He.

11. The method of claim 1, wherein the temperature of the reactants is maintained below the sintering temperature of the elemental material or alloy produced.

12. A method of continuously producing a non-metal or a metal or an alloy thereof comprising, providing a supply of halide vapor fluid, providing a supply of liquid alkali or alkaline earth metal, intimately mixing the halide vapor fluid with a liquid alkali metal or alkaline earth metal or mixtures thereof to produce the non-metal or the metal and the halide of the alkali or alkaline earth metal, said halide vapor being at a pressure not less than about 2 atmospheres and said alkali or alkaline earth metal being present in sufficient quantities to maintain the temperature of the reaction products less than the boiling point of the alkali metal or alkaline earth metal or

less than the sintering temperature of the non-metal or metal or alloy, whichever is less, to prevent the reaction product from depositing on the equipment, separating the solid metal or non-metal from the reactants, separating the alkali metal halide or the alkaline earth metal halide into its constituent parts, cooling and recycling the alkali metal or the alkaline earth metal to react with additional halide vapor.

13. The method of claim 12, wherein the reduction of halide to metal or non-metal is exothermic.

14. The method of claim 13, wherein the halide has a boiling point less than about 400°C.

15. The method of claim 14, wherein the halide vapor flows through the inner nozzle of concentric nozzles with the liquid metal flowing through the annulus formed by inner and outer nozzles, the vapor flow being sonic.

16. The method of claim 15, wherein the metal or non-metal is one or more of TiCl_4 , AlCl_3 , SbCl_3 , BeCl_2 , BCl_3 , TaCl_5 , VCl_4 , NbCl_5 , MoCl_4 , GaCl_3 , UF_6 , ReF_6 .

17. The method of claim 12, wherein the halide is one or more of Br and Cl.

Figure 1: Process Flow Diagram

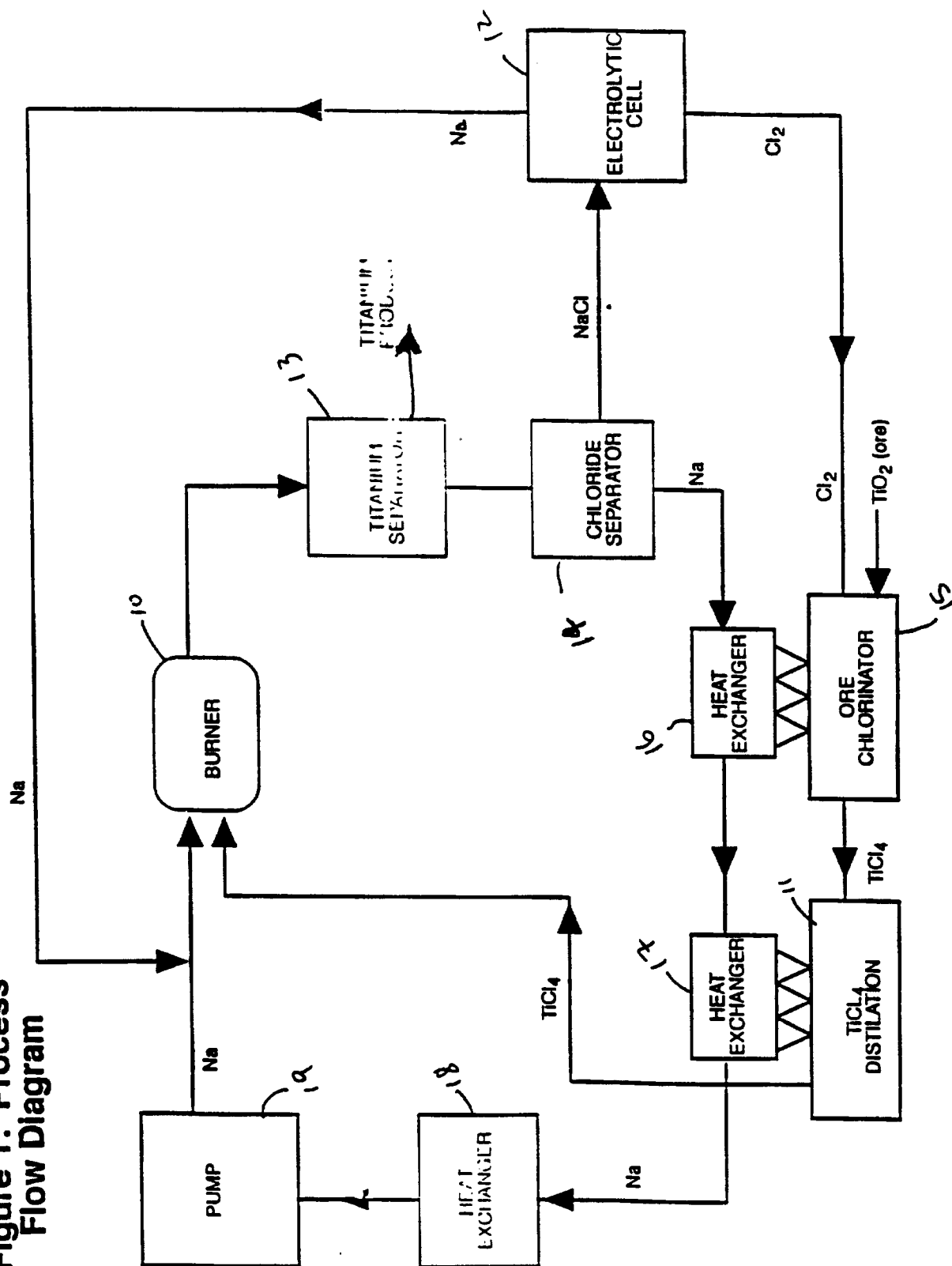
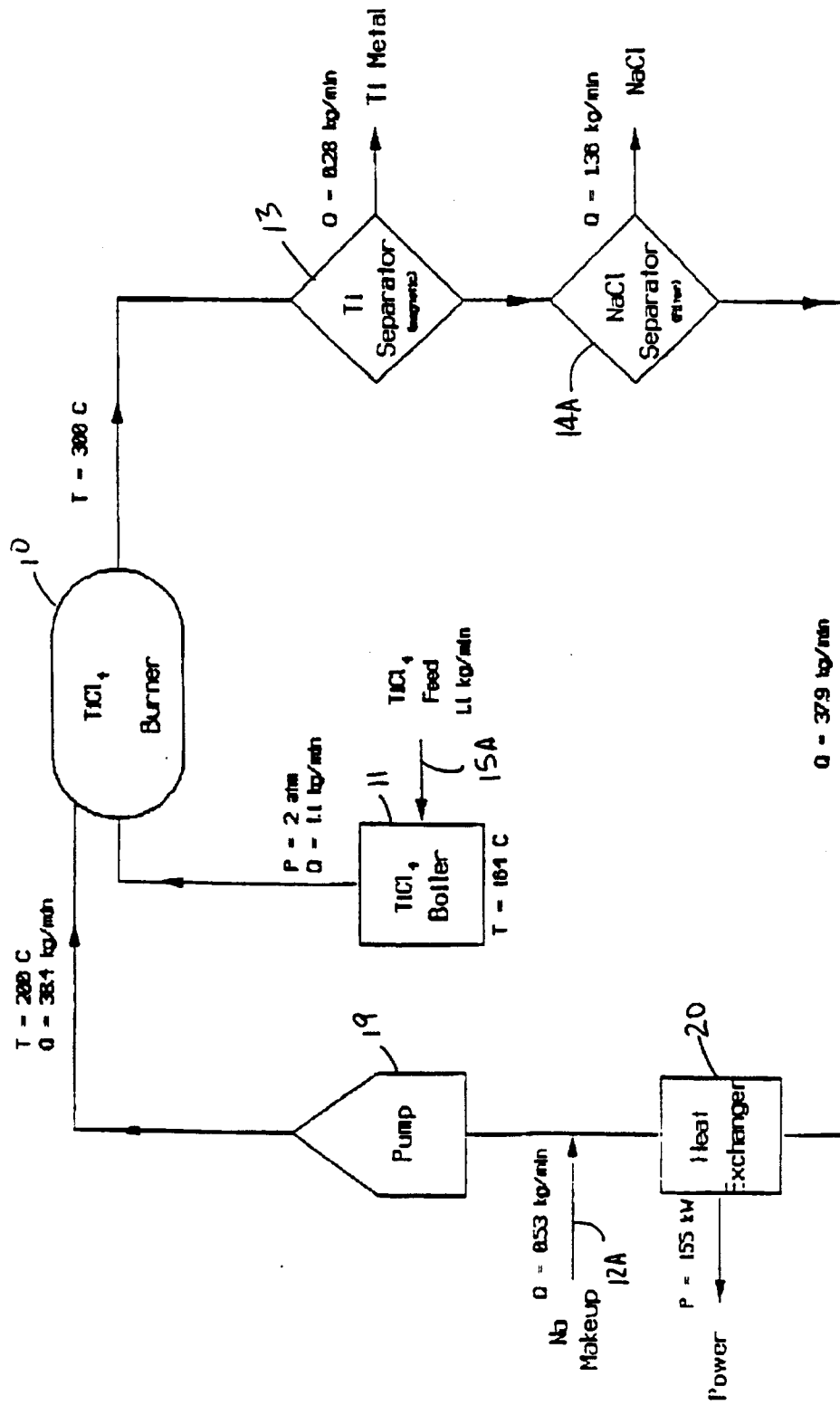


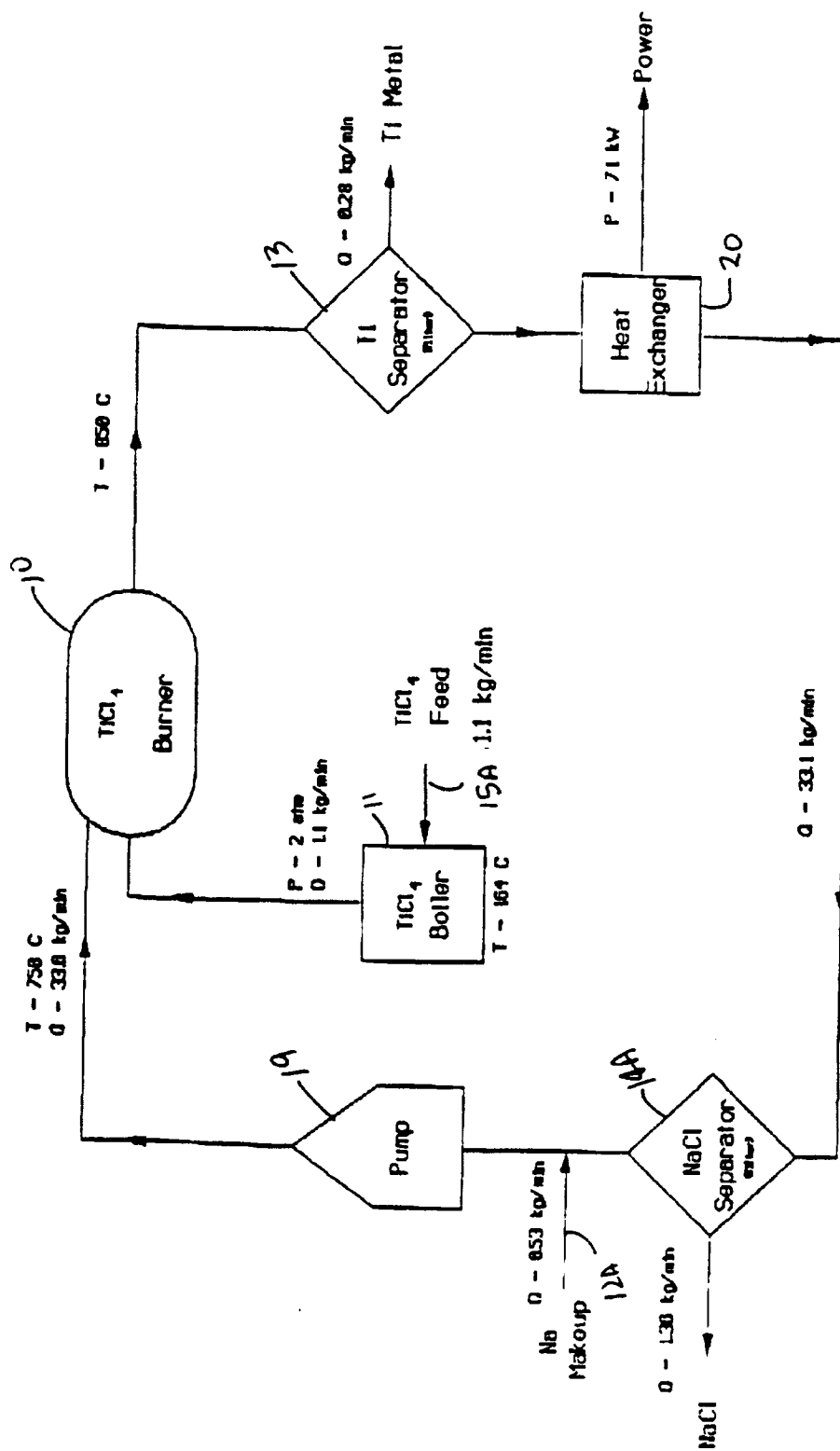
FIGURE 2



Low Temperature Process

basis : critical flow through 5 mm nozzle

Figure 3



High Temperature Process

basis : critical flow through 5 mm nozzle

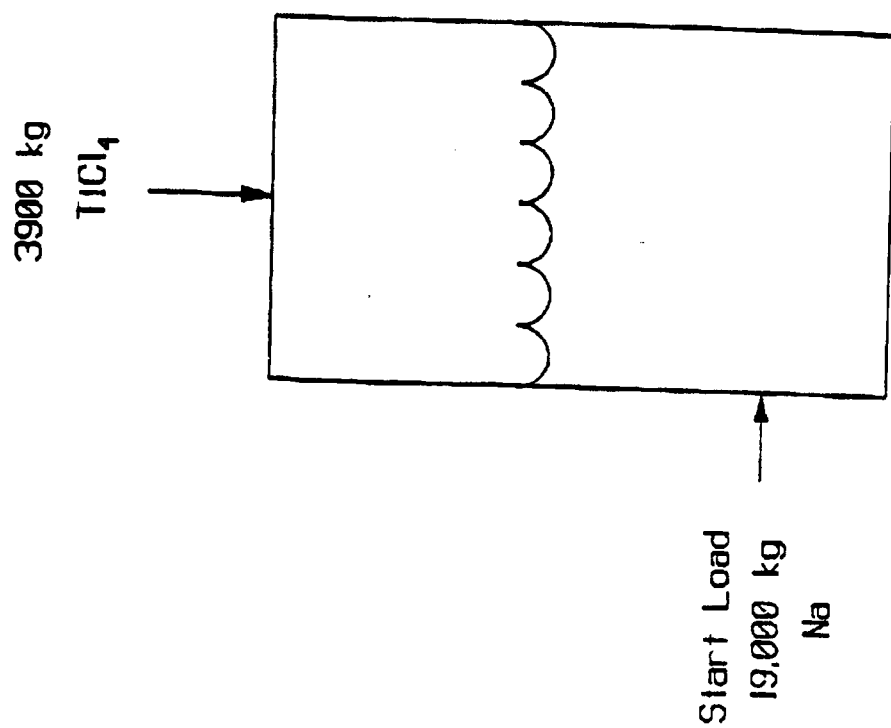


Figure 4

Batch Process

basis : 150 mtpy (same as continuous process)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/10159

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C22C 1/00, 24/00; C22B 4/00

US CL : 75/10.28, 344, 408, 589, 605, 613, 616, 619, 620, 676, 745

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 75/10.28, 344, 408, 589, 605, 613, 616, 619, 620, 676, 745

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS (search terms including the following: halide, alkali, and alkaline)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 2,205,854 (KROLL) 25 June 1940 col. 2, lines 12-15; 43-44 col. 7, lines 53-58; 60-68 col. 4, lines 34-43	1, 2, 4-7, 11
X	US, A, 4,445,931 (WORTHINGTON) 1 May 1984 col. 1, lines 6-10; 45-47; 51-60	1-11
--		-----
Y	col. 2, lines 17-52	12-17
Y	US, A, 3,825,415 (JOHNSTON et al.) 23 July 1974	12-17
Y	US, A, 3,535,109 (INGERSOLL) 20 October 1970	12-17

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A" document defining the general state of the art which is not considered to be part of particular relevance	*X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E" earlier document published on or after the international filing date	*Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*g"	document member of the same patent family
*O" document referring to an oral disclosure, use, exhibition or other means		
*P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

14 SEPTEMBER 1995

Date of mailing of the international search report

13 OCT 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3603

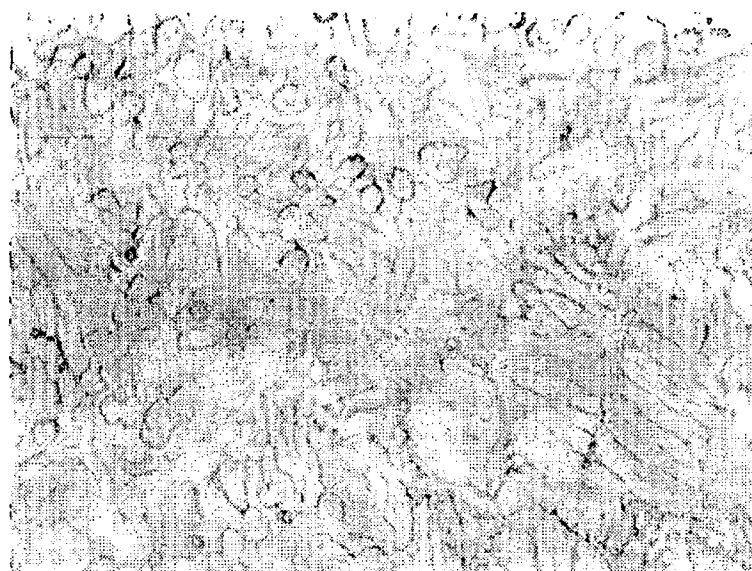
Authorized officer

SCOTT T. BLUNI

Telephone No. (703) 308-0441



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B22F 3/12, 3/14, 5/00, C22C 1/02, 1/05, 1/10, 14/00	A1	(11) International Publication Number: WO 98/24575 (43) International Publication Date: 11 June 1998 (11.06.98)
(21) International Application Number: PCT/US97/22030 (22) International Filing Date: 8 December 1997 (08.12.97) (30) Priority Data: 08/761,391 6 December 1996 (06.12.96) US (71) Applicant: DYNAMET TECHNOLOGY [US/US]; Eight A Street, Burlington, MA 01803 (US). (72) Inventors: ABKOWITZ, Stanley; 554 Lowell Street, Lexington, MA 02173 (US). ABKOWITZ, Susan, M.; 171 Swanton Street #29, Winchester, MA 01890 (US). WEIHRAUCH, Paul, F.; 169 Cypress Street, Newton, MA 02159 (US). HEUSSI, Harold, L.; 27 Addison Street, Essex, MA 01929 (US). ZIMMER, Walter; 16 Ball Hill Road, Princeton, MA 01541 (US). (74) Agents: GARRETT, Arthur, S. et al.; Finnegan, Henderson, Farabow, Garrett & Dunner, L.L.P., 1300 I Street, N.W., Washington, DC 20005-3315 (US).		(81) Designated States: CA, CN, JP, MX, RU, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: P/M TITANIUM COMPOSITE CASTING  500x		
(57) Abstract <p>A consumable billet for melting and casting a metal matrix composite component is made of a consolidated powder metal matrix composite having a titanium or titanium alloy matrix reinforced with particles. The preferred billet is a blended and sintered powder metal composite billet incorporating titanium carbide or titanium boride into a Ti-6Al-4V alloy.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

P/M TITANIUM COMPOSITE CASTING**BACKGROUND OF THE INVENTION****Field of the Invention**

This invention relates to titanium and titanium alloy metal matrix composite billets produced by powder metallurgy for use as melt starting stock to produce metal matrix composite articles by casting.

Description of the Related Art

Titanium has many properties that make it an attractive material for high performance applications. For example, it has one of the highest strength-to-weight ratios of the structural metals, and will form a thin, tough protective oxide film making it extremely oxidation resistant.

Titanium and titanium alloy metal matrix composites have been developed for applications requiring enhanced physical and mechanical properties. By incorporating ceramic or intermetallic particles in a titanium alloy matrix, improvements in strength, modulus, hardness and wear resistance have been achieved. These particulate reinforced metal matrix composites are typically manufactured using powder metallurgical (P/M) methods. Examples of P/M processes are described in U.S. Patents #4,731,115, #4,906,430, and #4,968,348, each of which is expressly incorporated herein by reference. To produce fully dense structural shapes, one preferred P/M process consists of blending pure titanium powder with appropriate ceramic or intermetallic materials in particulate form, together with alloying additions in either elemental or pre-alloyed powder form, then consolidating the blended powders in a controlled sequence: first, cold isostatic pressing, followed by vacuum sintering at elevated temperature and finally hot isostatic pressing. This CHIP process sequence results in a particulate reinforced metal matrix alloy in the form of a high density or fully dense solid, manufactured to a near-net shape.

Using this process, it is typically necessary to machine the P/M preform to achieve the final component shape and dimensions. Since machining requires a loss of starting material, and incurs significant costs associated with capital equipment, expensive tooling, labor and extended schedule, it is desirable to manufacture some titanium metal matrix composite components directly to the finished dimensions with little or no machining. Articles of titanium and titanium

alloys may be produced most economically and repeatably to near net shape by casting.

Castings of titanium and its alloys are typically made by vacuum arc remelting (VAR) process, wherein a consumable electrode billet of the desired alloy composition is progressively melted into the liquid state by an electric current flowing across a voltage potential in the form of a plasma arc. The alloy melts from the electrode tip and collects in a molten pool contained within a crucible. To chemically isolate the highly reactive molten metal from the crucible walls and thus avoid a source of contamination, the crucible walls are actively cooled so that the first molten metal in the crucible forms a solidified layer or "skull." This skull ensures that the molten titanium does not come into direct contact with the crucible, but rather only contacts other titanium metal, thereby minimizing contamination of the final product. After enough molten metal has been collected in the crucible or the electrode billet has been consumed, the liquid metal is poured into a casting mold, wherein the molten metal solidifies and takes on the desired final component shape and dimensions.

Other vacuum melting methods, such as vacuum induction melting (VIM), may be similarly employed to render titanium and titanium alloys molten prior to casting.

The powder metal composite billets of this invention may also serve as starting stock for these melt processes when casting titanium metal matrix composite articles.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a consumable billet for vacuum melting and casting a metal matrix composite component, made of a powder metal matrix composite consisting essentially of a titanium or titanium alloy matrix reinforced with particles.

Another aspect of the invention is drawn to a method of casting a particulate reinforced metal matrix composite article including the steps of providing a consolidated powder billet having a titanium metal matrix and particles dispersed therein, and melting the billet to cast the article.

Yet another aspect of the invention includes a cast titanium alloy metal matrix composite article strengthened by particles dispersed therein, the composite article

formed by melting a titanium metal matrix composite formed by consolidating powdered materials

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory, and are not restrictive of the invention as claimed.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is micrograph of a TiC reinforced titanium alloy casting produced from an electrode formed by powder metallurgy techniques.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The inventors have discovered that a sintered P/M titanium metal matrix composite electrode has significant advantages as the starting consumable billet stock, such as an electrode for vacuum arc melting and casting of near-net shape components. The composite electrode billet may be formed by, for example, cold isostatic pressing and sintering titanium alloy powders with additions of alloying elements and ceramic or intermetallic compounds in powder form. Another example of the billet manufacture is canning, evacuating, and hot isostatic pressing a powder blend of pre-alloyed powders and reinforcing particles.

The fine (e.g., 5 to about 100 microns) particulate reinforcement (e.g., a ceramic or intermetallic compound), once it enters the melt in the form of an incompletely melted solid particulate or a totally liquid entity, will act as a melt inoculant, serving as the nucleation site for the incipient solidification of the titanium alloy matrix, thus refining the resultant cast grain size, and reducing the tendency to develop matrix alloy segregation. In addition, since the composite alloy electrode material was created from uniformly blended fine powders by solid state diffusion bonding during vacuum sintering, the resultant cast material will be more chemically homogeneous and exhibit fewer gas-induced voids and porosity, than material produced by multiple VAR cycles from bulk (large in size and chemically inhomogeneous) alloying components. These microstructural features; gas porosity, large grain size and inhomogeneous distribution of alloying elements, are the most important factors responsible for the degraded properties of castings compared to their wrought or P/M equivalents.

From the point of view of manufacturing castings containing ceramic particles, it is typically difficult to distribute the particulate uniformly because of

usually large differences in density between the solid ceramic particle and the liquid matrix alloy, which causes the particles either to settle or to float. The selection of TiC, TiB, and/or TiB₂ as the reinforcing particles in titanium and titanium alloy castings minimizes the tendency of the particles to segregate in the casting because these compounds have nearly the same density as the most common titanium alloys. The reinforcing particles can be of a single compound, or mixed compounds of, for example, TiC and TiB particles. The carbide or boride compounds can either be introduced as discrete particles which do not dissolve, or dissolve very slightly in the molten titanium matrix. In another embodiment, carbides or borides can be produced in the final composite by introducing carbon- or boron-containing precursors that dissolve in the molten matrix material and precipitate out as, for example TiC, TiB or TiB₂, during solidification.

Furthermore, since the composite starting material is based on P/M fabrication methods, the process facilitates the introduction of innovative titanium matrix alloys. For example, it provides a means of incorporating matrix alloying additions, such as iron, copper, or nickel, that reduce the matrix melting point and range of temperatures over which matrix solidification occurs, and thereby further improve the castability of the metal matrix composite. Metal matrix powders are typically in the range of from 50 to about 250 microns. The metal matrix can be a single titanium alloy or a mixture of any number of titanium alloys. Examples of alloys that may be used include: alpha structure titanium materials such as commercially pure titanium, or near alpha Ti-5Al-2.5Sn, and Ti-8Al-1Mo-1V (unless otherwise indicated, as used herein, "alpha structure" includes both the alpha structure and the near alpha structure); alpha-beta alloys, such as Ti-6Al-4V, Ti-6Al-6V-2Sn or Ti-6Al-2Sn-4Zr-2Mo; or beta alloys (which, as used herein, include beta alloys, beta rich alloys and metastable beta alloys) such as Ti-13Zr-13Nb, Ti-1Al-8V-5Fe, Ti-15Mo-3Al-2.7Nb-0.25Sn and Ti-13V-11Cr-3Al.

In casting experiments, melting by either by vacuum induction or by vacuum arc processes, the vacuum sintered, P/M titanium alloy metal matrix composite starting stock produced pore-free and inclusion-free microstructures and mechanical strength properties as least as high as their CHIP-processed metal matrix composite equivalents. This is demonstrated by the as-cast microstructure shown in Fig. 1. The composite material shown in Fig. 1 had the following composition: 10%TiC in a

Ti-6Al-4V matrix. The sample was tested at room temperature to determine its tensile properties. The sample had a tensile strength of 160.1 ksi, a yield stress (0.2% offset) of 158.5 ksi, an elongation (over a gauge length of four times the diameter) percent of 0.2%, and a reduction in area of 1.8%.

A second sample having the same composition was also tested and had a tensile strength of 156 ksi, a yield stress (0.2% offset) of 155.2 ksi, an elongation (four times the diameter) percent of 0.2%, and a reduction in area of 2.4%. A third sample having the same composition had a Rockwell C hardness of 43.

It will be apparent to those skilled in the art that various modifications and variations can be made in the disclosed process and product without departing from the scope or spirit of the invention. For example, Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only.

WHAT IS CLAIMED IS:

1. A consumable billet for melting and casting a metal matrix composite article, said billet comprised of a powder metal matrix composite consisting essentially of a titanium or titanium alloy matrix reinforced with particles.
2. The consumable billet of claim 1, wherein the titanium metal matrix comprises an alpha titanium or alpha titanium alloy.
3. The consumable billet of claim 1, wherein the titanium metal matrix comprises an alpha-beta alloy.
4. The consumable billet of claim 1, wherein the titanium metal matrix comprises a beta alloy.
5. The consumable billet of claim 1, wherein said particles comprise intermetallic compounds.
6. The consumable billet of claim 1, wherein said particles are one or more additives selected from the group consisting of carbon, boron and precursor carbon- or boron-containing compounds that combine with titanium to form titanium carbides or titanium borides.
7. The consumable billet of claim 1, wherein said particles comprise ceramic materials.
8. The consumable billet of claim 1, wherein said particles comprise TiC particles.
9. The consumable billet of claim 1, wherein said particles comprise TiB particles.
10. The consumable billet of claim 1, wherein said particles comprise TiB₂ particles.
11. The consumable billet of claim 1, wherein said particles comprise TiC in combination with one or more of TiB and TiB₂ particles.
12. The consumable billet of claim 1, wherein said powder metal matrix composite is produced by cold isostatic pressing and vacuum sintering a powder blend consisting essentially of elemental titanium, reinforcing particles, and one or more of elemental and master alloy powders.
13. The consumable billet of claim 1, wherein said powder metal matrix composite is produced by canning, evacuating, and hot isostatic pressing a powder

blend consisting essentially of pre-alloyed powders of titanium alloys and reinforcing particles.

14. The consumable billet of claim 1, wherein said powder metal matrix composite consists essentially of 10 weight % TiC dispersed in a Ti-6Al-4V matrix.

15. A method of casting an article comprised of a particulate reinforced metal matrix composite, said method comprising the steps of:

providing a billet comprised of a consolidated powder and having a titanium metal matrix and particles dispersed therein, and

melting said billet to cast said article.

16. The method of claim 15, wherein the titanium metal matrix comprises an alpha titanium or alpha titanium alloy.

17. The method of claim 15, wherein the titanium metal matrix comprises an alpha-beta titanium alloy.

18. The method of claim 15, wherein said article consists essentially of 10 weight % TiC dispersed in a Ti-6Al-4V matrix.

19. The method of claim 15, wherein the titanium metal matrix comprises a beta alloy.

20. The method of claim 15, wherein the particles comprise TiC particles.

21. The method of claim 15, wherein the particles comprise TiB particles.

22. The method of claim 15, wherein the particles comprise TiB₂ particles.

23. The method of claim 15, wherein said particles are one or more additives selected from the group consisting of carbon, boron and precursor carbon- or boron-containing compounds, and

said additives combine with titanium to form titanium carbides or titanium borides.

24. The method of claim 15, wherein said particles comprise TiC in combination with one or more of TiB and TiB₂ particles.

25. The method of claim 15, wherein said melting is performed by a vacuum arc melting process.

26. The method of claim 15, wherein said melting is performed by a vacuum induction melting process.

27. The method of claim 15, further comprising producing said billet by cold isostatic pressing and vacuum sintering a powder blend consisting essentially

of elemental titanium, reinforcing particles, and one or more of elemental and master alloy powders.

28. The method of claim 15, further comprising producing said billet by canning, evacuating, and hot isostatic pressing a powder blend consisting essentially of pre-alloyed powders of titanium alloys and reinforcing particles.

29. A cast article comprising a titanium alloy metal matrix composite strengthened by particles dispersed therein, said cast article being formed by melting a titanium metal matrix composite formed by consolidating powdered materials.

30. The cast article of claim 29, wherein the titanium metal matrix comprises an alpha titanium or alpha titanium alloy.

31. The cast article of claim 29, wherein the titanium metal matrix comprises an alpha-beta alloy.

32. The cast article of claim 29, wherein the titanium metal matrix comprises a beta alloy.

33. The cast article of claim 29, wherein said particles comprise intermetallic compounds.

34. The cast article of claim 29, wherein said particles are one or more additives selected from the group consisting of carbon, boron and precursor carbon- or boron-containing compounds that combine with titanium to form titanium carbides or titanium borides.

35. The cast article of claim 29, wherein said particles comprise ceramic materials.

36. The cast article of claim 29, wherein said particles comprise TiC particles.

37. The cast article of claim 29, wherein said particles comprise TiB particles.

38. The cast article of claim 29, wherein said particles comprise TiB₂ particles.

39. The cast article of claim 29, wherein said particles comprise TiC in combination with one or more of TiB and TiB₂ particles.

40. The cast article of claim 29, wherein said powder metal matrix composite is produced by cold isostatic pressing and vacuum sintering a powder

blend consisting essentially of elemental titanium, reinforcing particles, and one or more of elemental and master alloy powders.

41. The cast article of claim 29, wherein said powder metal matrix composite is produced by canning, evacuating, and hot isostatic pressing a powder blend consisting essentially of pre-alloyed powders of titanium alloys and reinforcing particles.

42. The cast article of claim 29, wherein said powder metal matrix composite consists essentially of 10 weight % TiC dispersed in a Ti-6Al-4V matrix.

43. The cast article of claim 29, wherein said melting is performed by a vacuum arc melting process.

44. The cast article of claim 29, wherein said melting is performed by a vacuum induction melting process.

1/1

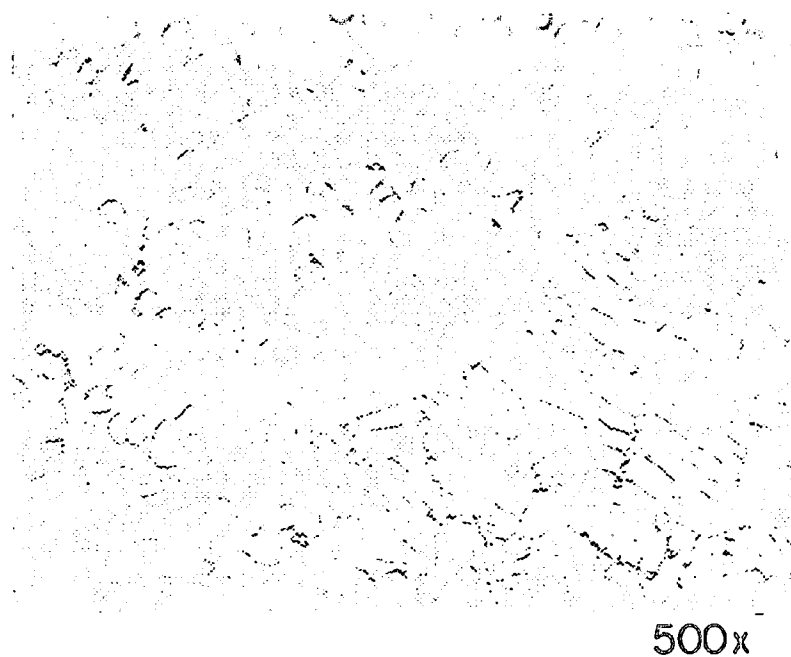


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/22030

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) :B22F 3/12, 3/14, 5/00; C22C 1/02; 1/05, 1/10, 14/00 US CL :75/230, 245; 164/47, 469, 474; 420/417 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 75/230, 245; 164/47, 469, 474; 420/417 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,409,518 A (SAITO et al) 25 April 1995.	
A	US 5,545,248 A (TOKUMOTO et al) 13 August 1996.	
A	US 4,731,115 A (ABKOWITZ et al) 15 March 1988.	
A	US 4,906,430 A (ABKOWITZ et al) 6 March 1990.	
A	US 4,582,679 A (WILSON et al) 15 April 1986.	
A	US 4,601,874 A (MARTY et al) 22 July 1986.	
A	US 5,102,451 A (ABKOWITZ et al) 7 April 1992.	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
26 MARCH 1998	27 APR 1998	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer DANIEL JENKINS	
Facsimile No. (703) 305-3230	Telephone No. (703) 306-4157	

INTERNATIONAL SEARCH REPORT**International application No.**
PCT/US97/22030

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,909,840 A (SCHLUMP) 20 March 1990.	

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



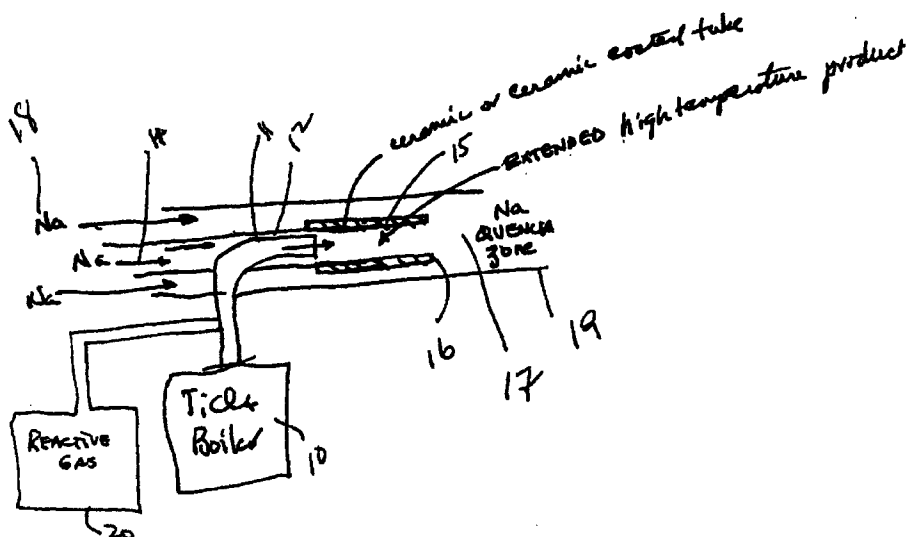
(43) International Publication Date
18 March 2004 (18.03.2004)

PCT

(10) International Publication Number
WO 2004/022269 A2

- (51) International Patent Classification⁷: **B22F 9/28**
- (21) International Application Number:
PCT/US2003/027391
- (22) International Filing Date:
3 September 2003 (03.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/408,683 7 September 2002 (07.09.2002) US
60/408,926 7 September 2002 (07.09.2002) US
60/411,328 17 September 2002 (17.09.2002) US
- (71) Applicant (*for all designated States except US*): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US]; 20634 W. Gaskin Drive, Lockport, IL 60441 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **ANDERSON, Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). **ARMSTRONG, Donn** [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: METHOD AND APPARATUS FOR CONTROLLING THE SIZE OF POWDER PRODUCED BY THE ARMSTRONG PROCESS



(57) Abstract: A method of controlling the size and morphology of powder made by the subsurface injection of a halide vapor into a liquid metal is disclosed. A reaction zone is established and the temperature thereof or the time the powder remains therein is controlled to change powder characteristics.

WO 2004/022269 A2

METHOD AND APPARATUS FOR CONTROLLING THE SIZE OF POWDER PRODUCED BY THE ARMSTRONG PROCESS

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application U.S. Provisional Application Serial No. 60/411,328 Filed September 17, 2002, U.S. Provisional Application Serial No. 60/408,926, Filed September 7, 2002 and U.S. Provisional Application Serial No. 60/408,683, Filed September 7, 2002

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong Process as described in U.S. Patent Nos. 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. When the above-captioned patents were filed, it was understood that the steady state reaction temperature could be varied depending upon the amount of excess liquid metal or the ratio of liquid metal to halide being reduced. For instance, the above-identified patents taught that using a greater excess of the liquid metal beyond the stoichiometric amount required for the reaction would produce a lower steady state reaction temperature and similarly, diluting or reducing the amount of halide introduced into the liquid metal would also reduce the steady state operating temperature of the process. However, there was no appreciation of the nature of what occurred at the reaction zone, as separate from down stream conditioning, and no appreciation that the particle size of the powder produced could be controlled by manipulating various parameters in the reaction zone.

Although the above referenced patents disclose that powder is produced having average size distributions in the range of from about 0.1 micron to about 10 microns, in fact what was produced was not controllable but was whatever happened to be produced according to the parameters of the reaction. Powder morphology has been discovered to be an important factor in the production of powder. Moreover, larger diameter powders have larger packing fractions and the control of the powder morphology has become an important aspect in the

development of the Armstrong Process. It has been discovered that powder morphology is affected by a number of parameters including the temperature of the reaction zone, the length of time that the material stays in the reaction zone.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to control powder morphology during the production of powder by the Armstrong Process.

Yet another object of the present invention is to control the temperature of reactants in the reaction zone.

Yet another object of the present invention is to provide a method of controlling the morphology of the powder produced with the Armstrong Process in which the temperature of the reaction products in the reaction zone and the time in which the products remain in the reaction zone are manipulated to control the size of the powder produced by the reaction.

Another object of the present invention is to control the temperature of the reaction products in the reaction zone by varying one or more of the pressure of the reaction zone, the constituents of the reaction zone and the time that the constituents remain in the reaction zone.

Still another object of the present invention is to control the temperature of the reactants in the reaction zone by means of controlling the reactants in the reaction zone by adding a reactive gas to the reaction zone.

Yet another object of the present invention is to provide an apparatus for controlling the morphology of the powder during the practice of the Armstrong invention in which the amount of excess liquid metal reductant is controlled during the reaction and subsequent thereto for quenching purposes.

A final object of the present invention is to provide an apparatus of the type set forth in which a gas injection nozzle is surrounded with a sleeve forming an annulus extending axially of a conduit providing liquid metal flow so as to control the amount of liquid metal present in the reaction zone and yet provide a substantial increase in the amount of liquid metal downstream of the reaction zone.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly

pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantage of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of an apparatus for practicing the invention.

DETAILED DESCRIPTION OF THE INVENTION

By limiting the amount of excess sodium to which the reaction products are exposed the temperature of the reaction products can be maintained at a higher temperature for a longer period of time than possible if the reaction products are immediately exposed to large excess of sodium as soon as the reaction products are formed. By enclosing the reaction zone within a material such as a refractory and keeping the reaction products separated from large excess liquid metal which cools the reaction products by absorbing the heat of reaction, less cooling occurs and a longer high temperature reaction zone is obtained. By longer high temperature reaction zone, we mean a few inches where the temperatures of the reaction products are very high. Extending the high temperature zone prior to cooling the reaction products of salt and powder with additional liquid metal allows the powder particles to coalesce forming larger particles. There is a relationship between the time particles spend at elevated temperatures and the particle size. The reaction products could, if the excess sodium present was very small, reach very high temperatures at which steel or even titanium may fail. A ceramic environment can contain reaction products at high temperatures permitting larger particles to form. Any ceramic which is non-reactive with the reaction products at the reaction temperatures (for instance, such as a yttria tube or a metal tube with an interior surface of yttria, such as a tungsten tube internally coated with yttria) is

applicable to the invention.

It is now believed that the reaction zone is a bubble containing vapor of the liquid reducing metal and liquid as well as vapor of the salt produced and the product powders. The upper limit of the temperature within the reaction zone is the boiling point of the salt produced by the reaction, for so long as liquid salt remains the phase change from liquid salt to vapor soaks up sufficient heat that the temperature will not exceed the salt boiling point. However, if all salt is in the vapor phase, then the temperature within the reaction zone can increase to the melting point of the produced powder.

We have determined that reaction zone temperature as well as the time at which reaction products are retained at reaction zone temperatures control to some degree, the morphology of the produced powder. There are a variety of conditions or combination of conditions which enable us to control reaction zone temperature and residence time of the produced powder in the reaction zone.

The temperature of the reaction zone can be controlled by increasing the pressure at which the reaction occurs or by adding a reactive gas, such as a halide, preferably chlorine, or by limiting the amount of reducing metal in the reaction zone. Duration in the reactor zone can be controlled by the length of the reaction zone, all as will be described, and various combinations may also be used.

Referring to Figure 1, as an example only, TiCl_4 from a boiler 10 flows as a vapor through a nozzle 11 into a stream 14 of sodium contained in a tubular reactor 12. By virtue of the flow rates of the TiCl_4 and sodium the amount of excess sodium over stoichiometric is kept small so that the temperature of the reaction products is high. A ceramic tube 15 or metal tube having an internal surface of ceramic or other high temperature material contains the high temperature reaction products and extends the time at which the reaction products remain at high temperature before the reaction products exit the tube 15 at the end 16 thereof to encounter a large excess of liquid sodium in a quench zone 17 formed by sodium 18 contained in a larger tube or reactor 19.

Although illustrated with TiCl_4 and sodium, the invention applies to any material made by the exothermic reduction of a halide gas with a reductant metal as

taught in the patents referenced above. To add a reactive gas, a source 20 is in fluid communication with the chloride vapor being reduced.

In the process taught in the above-referenced patents, the temperature in the reaction zone is limited by the phase changes of the material in the reaction zone produced such as the salt or the reductant metal or the produced elemental material or alloy. In the examples disclosed in the referenced patents, the reaction product stream contains a slurry of excess liquid sodium and solid sodium chloride and solid titanium powder. While the boiling point of the sodium chloride is higher than the boiling point of the sodium and lower than the melting point of titanium, in the reaction zone, as stated, in sodium vapor. NaCl liquid and vapor and titanium solid. Therefore, in order to increase the temperature of the reaction zone above the boiling point of sodium chloride (1662°C) to the melting point of titanium at 1668°C, the boiling point of the sodium chloride needs to be raised so that it equals or exceeds the melting point of the titanium. If the boiling point of the reductant metal (such as sodium) and the produced salt (such as NaCl) is raised above the melting point of the produced elemental material (such as Ti) or alloy, the element material (such as Ti) or alloy or ceramic particles produced can melt and coalesce, thereby forming larger particles with smaller surface areas and higher packing fractions. If the control of the reaction zone temperature is accomplished by operating the reaction zone under pressure so that the boiling point of the produced salt (NaCl) exceeds the melting point of the produced elemental material or alloy (titanium), the pressure required to increase the boiling point of NaCl above the melting point of Ti is not large. Pressures in the range of from about 14 psig to about 150 psig are useful to make powder having diameters in the 0.1 to about 20 μ micron range. Moreover, particularly, 2-3 atmospheres effectively raise the boiling point of NaCl to requisite temperatures.

Therefore, the process of the present invention controls the size, surface area and packing fraction of particles produced by the method disclosed in the above identified patents by increasing the pressure in the reaction zone to control the temperature of the materials in the reaction zone so that the melting point of the produced metal is lower than the boiling point of the produced salt.

In the process disclosed in the referenced patents, the limit of the temperature in the reaction zone is the boiling point of the highest boiling material in the reaction zone which exists in two phases. For instance, in the process specifically described by way of example only in the referenced patent, TiCl_4 reduced by liquid Na produces NaCl and Ti solids in the presence of excess liquid Na. So long as liquid sodium is present, the reaction temperature will not exceed the boiling point of Na or 892°C. After all the liquid Na has been vaporized, the NaCl, now molten, will begin to boil and its boiling point of 1465°C at one atm will limit the reaction zone temperature. Because the boiling point of NaCl 1465°C at one atm is lower than the melting point of Ti (1662°C), the temperature in the reaction zone will remain below the Ti melting point, as long as liquid NaCl is present. Raising the pressure in the range of from about 2 to about 3 atmospheres, increases the boiling point of the NaCl, permitting the temperature in the reaction zone to increase.

By adding a reactant gas such as chlorine to the reaction chamber in which titanium tetrachloride is reduced by sodium, such as by combining chloride gas with the TiCl_4 , the temperature of the reaction products can be raised beyond the boiling point of sodium chloride so that the titanium particles produced will melt, coalesce and become larger. The reactant gas must contribute more energy to the reaction than it absorbs or the invention will not have its intended result. Moreover, the reactant gas should be selected to avoid adding unwanted impurities to the produced elemental material or alloy thereof. Additions of chlorine in the range of from about 90 mole percent to about 200 mole percent of the halide being reduced will provide increased temperature in the reaction zone.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A method of controlling the size of powder produced from the reduction of a halide vapor by a liquid alkali metal or a liquid alkaline earth metal or mixtures thereof to produce a slurry of a powder and salt in excess liquid alkali or alkaline earth metal or mixtures thereof, comprising establishing a reaction zone by introducing a halide vapor into a liquid alkali or alkaline earth metal causing an exothermic reaction, the reaction zone including vapor of an alkali metal or an alkaline earth metal or mixtures thereof and vapor of the salt produced by the exothermic reaction, controlling one or both of the temperature of the reaction products in the reaction zone and the time during which the reaction products are maintained in the reaction zone to vary the size of the powder, whereby increasing the temperature of the reactants in the reaction zone and/or the length of time of the reactants in the reaction zone increases the size of the powder within the range of from about 0.1 micron to about 20 microns.
2. The method of claim 1, wherein the powder is a ceramic.
3. The method of claim 2, wherein the ceramic is a nitride or a carbide.
4. The method of claim 1, wherein the powder includes one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re or Si.
5. The method of claim 2, wherein the liquid metal is Na or Mg and the halide is a chloride.
6. The method of claim 5, wherein the temperature of the reactants in the reaction zone may also be controlled by controlling the volume percent of the reductant metal vapor in the reaction zone.
7. The method of claim 6, wherein the reaction zone is operated at a pressure in the range of from about 14 psig to about 150 psig.
8. The method of claim 7, wherein the temperature of the reactants in the reaction zone is controlled by the boiling point of the salt vapor in the reaction zone.
9. The method of claim 1A, wherein the reaction zone is operated above atmospheric pressure.
10. The method of claim 1, wherein the percentage of alkali metal or alkaline earth metal vapor in the reaction zone is controlled to vary the temperature

of the contents of the reaction zone.

11. The method of claim 1, wherein a reactive gas in addition to the halide being reduced is present in the reaction zone to increase the temperature of the contents thereof.

12. The method of claim 11, wherein the reactive gas is a halide or mixture thereof.

13. The method of claim 12, wherein the reactive gas is chlorine.

14. The method of claim 13, wherein the chlorine is present in the range of from about 90 mole percent to about 200 mole percent of the halide being reduced.

15. The method of claim 1, wherein the boiling point of the salt in the reactive zone is controlled to be equal to or greater than the melting point of the powder in the reaction zone.

16. The method of claim 1, wherein the reaction zone is confined by a ceramic surface and upon exit from the ceramic surface the reactants are introduced into excess alkali and/or alkaline earth liquid metal to cool the reactants.

17. A powder having preselected diameters within the range of from about 0.1 to about 20 microns produced by the method of claim 1.

18. A solid object produced with the powder of claim 1.

19. The method of claim 18, wherein the reaction zone is a bubble.

20. The method of claim 19, wherein the boiling point of the salt in the reaction zone is controlled to determine the maximum temperature of the contents in the reaction zone and to vary the size of the metal powder.

21. The method of claim 20, wherein the reaction zone is operated above atmospheric pressure.

22. The method of claim 20, wherein the reaction zone is operated in the range of from about 14 psig to about 150 psig.

23. The method of claim 20, wherein the percentage of alkali metal or alkaline earth metal vapor in the reaction zone is controlled to vary the temperature of the contents of the reaction zone.

24. The method of claim 20, wherein a reactive gas in addition to the halide being reduced is present in the reaction zone to increase the temperature of the

contents thereof.

25. The method of 20 claim, wherein the reactive gas is a halide or mixture thereof.

26. The method of claim 1, wherein the reactive gas is chlorine.

27. The method of claim 26, wherein the chlorine is present in the range of from about 90 mole percent to about 200 mole percent of the halide being reduced.

28. The method of claim 20, wherein the boiling point of the salt in the reactive zone is controlled to be equal to or greater than the melting point of the metal powder in the reaction zone.

29. The method of claim 20, wherein the reaction zone is confined by a ceramic surface and upon exit from the ceramic surface the reactants are introduced into excess alkali and/or alkaline earth liquid metal to cool the reactants.

30. The method of claim 29, wherein the ceramic surface is yttria.

31. The method of claim 30, wherein the ceramic surface is a tube.

32. The method of claim 20, wherein the powder includes one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re or Si.

33. A powder having preselected diameters within the range of from about 0.1 to about 20 microns produced by the method of claim 20.

34. A solid object produced with the powder of claim 18.

35. A method of controlling the size of metal powder produced from the reduction of a halide vapor by a liquid alkali metal or a liquid alkaline earth metal or mixtures thereof to produce a slurry of a metal powder and salt in excess liquid alkali or alkaline earth metal or mixtures thereof, comprising establishing a reaction zone by introducing a halide vapor into a liquid alkali or alkaline earth metal causing an exothermic reaction, the reaction zone including vapor of an alkali metal or an alkaline earth metal or mixtures thereof and vapor of the salt produced by the exothermic reaction, controlling one or more of the temperature of the reaction products in the reaction zone and the time during which the reaction products are maintained in the reaction zone and the volume percent of vapor of the alkali metal or the alkaline earth metal to vary the size of the metal powder, whereby increasing the temperature of the reactants in the reaction zone and/or the length of time of the

reactants in the reaction zone and/or decreasing the volume percent of the metal vapor in the reaction zone increases the size of the metal powder within the range of from about 0.1 micron to about 20 microns.

36. The method of claim 35, wherein the boiling point of the salt in the reaction zone is controlled to determine the maximum temperature of the contents in the reaction zone and to vary the size of the metal powder.

37. The method of claim 36, wherein the reaction zone is operated above atmospheric pressure.

38. The method of claim 37, wherein the reaction zone is operated in the range of from about 14 psig to about 150 psig.

39. The method of claim 38, wherein a reactive gas in addition to the halide being reduced is present in the reaction zone to increase the temperature of the contents thereof.

40. The method of claim 39, wherein the reactive gas is a halide or mixture thereof.

41. The method of claim 40, wherein the reactive gas is chlorine.

42. The method of claim 41, wherein the chlorine is present in the range of from about 90 mole percent to about 200 mole percent of the halide being reduced.

43. The method of claim 37, wherein the boiling point of the salt in the reactive zone is controlled to be equal to or greater than the melting point of the metal powder in the reaction zone.

44. The method of claim 37, wherein the reaction zone is confined by a ceramic surface and upon exit from the ceramic surface the reactants are introduced into excess alkali and/or alkaline earth liquid metal to cool the reactants.

45. The method of claim 18, wherein the powder includes one or more of Ti, Al, Sb, Be, B, Ta, V, Nb, Mo, Ga, U, Re or Si.

46. A powder having preselected diameters within the range of from about 0.1 to about 20 microns produced by the method of claim 37.

47. A solid object produced with the powder of claim 37.

48. An apparatus for continuously producing powder from the reduction of a halide vapor by a liquid alkali metal or alkaline earth metal or mixtures thereof to

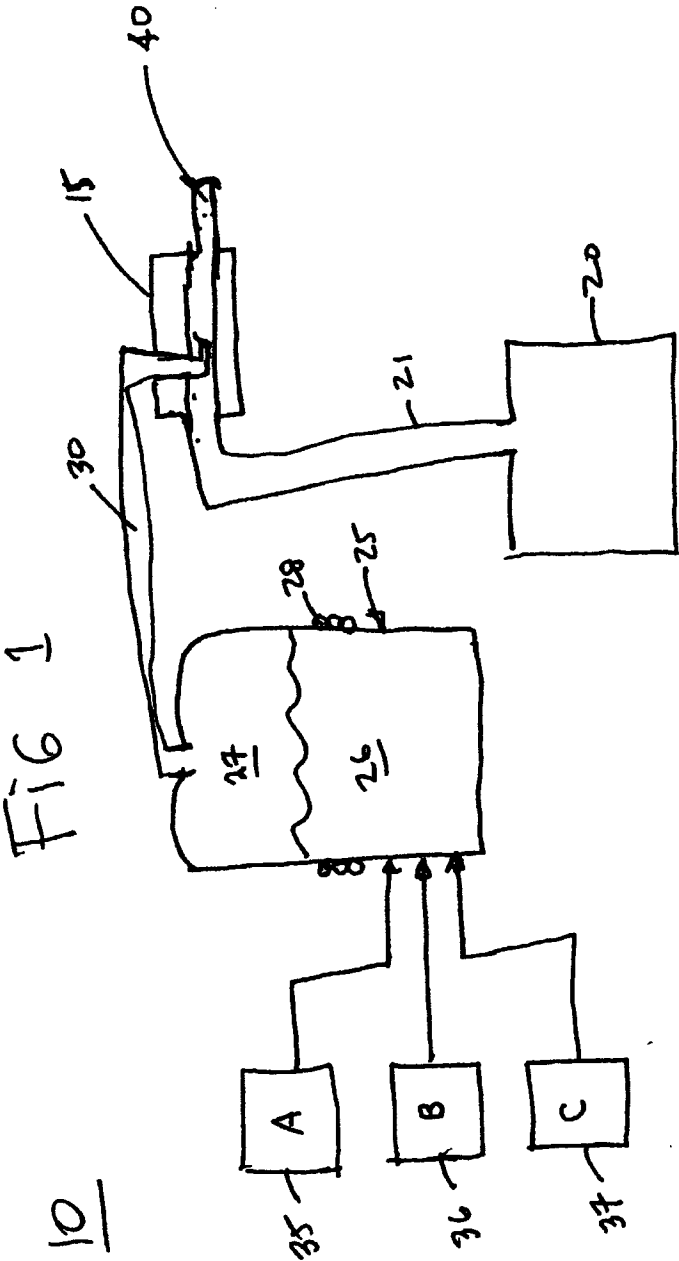
produce a slurry of a powder and salt in excess liquid alkali metal or alkaline earth metal or mixtures thereof, comprising a gas injection nozzle in communication with a supply of halide vapor to be reduced and having an open end, and a proportioning device in communication with a supply of liquid reductant metal and said gas injection nozzle providing a first portion of liquid reductant metal into which the halide gas to be reduced is injected through said gas injection nozzle and providing a second larger portion of liquid reductant metal into which the reaction production of the halide gas and the first portion of reductant metal are introduced to cool the reaction products forming a slurry therewith.

49. An apparatus for continuously producing powder from the reduction of a halide vapor by a liquid alkali metal or alkaline earth metal or mixtures thereof to produce a slurry of a powder and salt in excess liquid alkali metal or alkaline earth metal or mixtures thereof, comprising a gas injection nozzle in communication with a supply of halide vapor to be reduced and having an open end, a conduit in communication with a supply liquid reductant metal surrounding at least a portion of said gas injection nozzle, a sleeve surrounding at least a portion of said gas injection nozzle forming an annulus therewith extending axially of said conduit to provide a flow path for a predetermined quantity of liquid reductant metal to flow therethrough and into which is injected the halide vapor to be reduced through said gas injection nozzle causing an instantaneous exothermic reaction producing powder and salt reaction products, the reaction products flowing from said sleeve into liquid reductant metal in said conduit cooling the reaction products and forming a slurry of powder and salt in excess liquid alkali metal or alkaline earth metal or mixtures thereof.

50. The apparatus of claim 49, wherein said sleeve has an interior ceramic surface.

51. The apparatus of claim 50, wherein the predetermined quantity of liquid reductant metal is less than 50 times the stoichiometric quantity needed for the reduction of the halide vapor.

52. The apparatus of claim 51, and further comprising a pump in communication with said gas injection nozzle and the supply of halide vapor for injecting the halide vapor into the liquid metal at greater than sonic velocity.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
18 March 2004 (18.03.2004)

PCT

(10) International Publication Number
WO 2004/022797 A1

(51) International Patent Classification⁷: **C22B 34/12**,
B22F 9/28

(74) Agent: **LEVY, Harry, M.**; Emrich & Dithmar, 300 South
Wacker Drive, Suite 3000, Chicago, IL 60606 (US).

(21) International Application Number:
PCT/US2003/027390

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date:
3 September 2003 (03.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/408,934 7 September 2002 (07.09.2002) US

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicants (*for all designated States except US*): **INTER-
NATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).
JACOBSEN, Lance [US/US]; 123 San Carlos Road,
Minooka, IL 60447 (US).

Published:

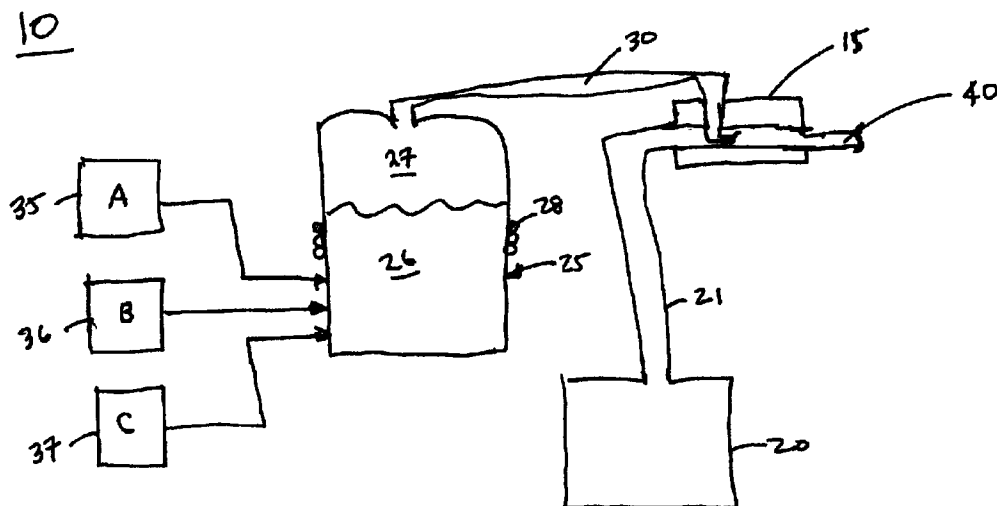
- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **ANDERSON,
Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills,
IL 60514 (US). **ARMSTRONG, Donn** [US/US]; 6005
Ridge Court, Lisle, IL 60532 (US).

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: PREPARATION OF ALLOYS BY THE ARMSTRONG METHOD



(57) Abstract: A method and apparatus for making alloys or ceramics by the subsurface injection of equilibrium mixed halide vapor of a boiling liquid of the ceramic or alloys constituents into liquid alkali or alkaline earth metals or mixtures thereof is disclosed. Various powders and products are disclosed.

WO 2004/022797 A1

PREPARATION OF ALLOYS BY THE ARMSTRONG METHOD**RELATED APPLICATIONS**

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application U.S. Provisional Application Serial No. 60/408,934 filed September 7, 2002.

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong process as described in U.S. patents 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. As disclosed in the above-three patents, alloys or ceramics can be prepared by establishing a mixture of gases which are fed, as disclosed in the above-referenced patents, subsurface to a reducing metal thereby to initiate the reduction of the gas mixture to the corresponding alloy or ceramic. In general, the most obvious way to provide the mixed vapor is to introduce the constituent vapors in the required atomic ratio to a manifold and feed the mixed material to the reducing metal.

The present invention relates to another means for mixing the alloy or ceramic constituents prior to the introduction of the mixed vapor to the reducing metal. In the present invention, the various constituents of the alloy or ceramic are initially mixed as a liquid which is thereafter boiled. After the liquid is boiled and reaches equilibrium, the vapor coming off the liquid has the same atomic ratio as the feed liquid to the boiler, which may or may not be different than the liquid in the boiler. At steady state, the vapor from the boiler can be fed to the Armstrong process in the same manner as illustrated in the three referenced patents to produce an alloy or ceramic having a constant atomic ratio.

This invention simplifies the handling of materials, and particularly those materials such as aluminum chloride which sublime rather than boil. For those materials, the solid is heated in a vessel under pressure so that a liquid is formed and that liquid is thereafter transmitted to a boiler, as will be shown. By way of example a boiler having feed streams of aluminum chloride and vanadium chloride and titanium chloride in atomic ratios of 6% Al and 4%V and the remainder Ti will produce at equilibrium a vapor of 6% Al, 4%V and 90% Ti, even if the atomic ratios of the

constituents of the liquid in the boiler differ. Using the equilibrium vapor as a feed in the process disclosed in the referenced patents produces a 6% Al, 4%V, titanium alloy.

The invention applies to a wide variety of alloys or ceramics and simplifies the materials handling of the constituent parts of each alloy produced in the Armstrong Process.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method and apparatus of producing an alloy or ceramic in which the liquid constituents thereof are fed into a boiler and the equilibrium vapor therefrom is thereafter used in the subsurface reduction with a liquid alkali or alkaline earth metal to form the alloy or ceramic.

Yet another object of the present invention is to provide a method of producing an alloy or ceramic by the exothermic subsurface reduction of a mixed halide vapor of the alloy or ceramic constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy or ceramic constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter introducing the equilibrium vapor into the liquid reductant metal to form an alloy or ceramic powder of the equilibrium vapor constituents in the preselected atomic ratio.

Still a further object of the present invention is to provide a method of producing an alloy by the exothermic subsurface reduction of a mixed halide vapor of the alloy constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter injecting the equilibrium vapor into the liquid reductant metal at greater than sonic velocity to form an alloy powder of the equilibrium vapor constituents in the preselected atomic ratio.

Another object of the present invention is to provide an apparatus for practicing the method hereinbefore discussed.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the

details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of the apparatus and system for practicing the method of the present invention.

DETAIL DESCRIPTION OF THE PREFERRED EMBODIMENT

Figure 1 illustrates a system 10 having a reactor 15 in communication with a source 20 of liquid reductant metal connected to the reactor by a pipe 21.

A boiler 25 has therein a liquid 26 which when boiled produces at equilibrium a vapor 27 which is introduced via pipe 30 into the pipe 21 preferably but not necessarily carrying a flowing stream the liquid metal from the source thereof 20, thereby producing a slurry 40 of the same type, consisting of excess liquid metal, ceramic or metal powder and a salt produced during the reaction as discussed in the above referenced Armstrong et al. patents.

The boiler 25 is provided with a heat source such as coils 28 and is connected or in communication with a plurality of sources of the constituents of the ultimately produced alloy or ceramic. Three such sources 35, 36, and 37 being illustrated.

The advantage of the present invention is that during the production of a ceramic or an alloy by the Armstrong method, liquid handling is frequently easier and more efficacious than handling vapors. To this end, representative constituent sources 35, 36 and 37 can each be a vessel (pressurized or not) in which the individual constituent halide is maintained as a liquid and thereafter transferred in a suitable predetermined atomic ratio into the boiler 25. The atomic ratio of the constituents from each of the sources 35, 36 and 37 determines the atomic ratio of the constituents in the vapor 27 at equilibrium with the liquid 26. Thereafter, the equilibrium vapor 27 in the preselected and predetermined atomic ratios is injected subsurface into a stream of liquid metal at

greater than sonic velocity, as is taught in the above-referenced Armstrong patents.

Although the reductant metal may be any suitable alkali or alkaline earth metal or mixtures thereof, the preferred reductant metal is sodium or magnesium, the most preferred reductant metal being sodium. Although a variety of halides may be used, the preferred halide is a chloride due to availability and cost. Although frequently described with respect to titanium, the invention is in fact applicable to a wide variety of alloys and ceramics, particularly ceramics including a nitride, a carbide, or a boride or mixtures thereof. In addition, many alloys may be produced by the method and apparatus of the subject invention, particularly those alloys or ceramics that include one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si. More preferably, alloys or ceramics are produced which include one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.

Moreover, the powder ceramics or alloys produced by the method and apparatus of the present invention are useful in a wide variety of processes to make many different products. For instance, various powder metallurgy techniques may be used to produce product from the powder made by the method and apparatus of the present invention. Moreover, a wide variety of alloy and ceramic powders may be either melted or compressed to form a solid from the powder of the present invention. A particularly important alloy at the present time is the 6:4 alloy of titanium. This alloy is widely used in aerospace and defense and is substantially 6% aluminum and 4% vanadium with the remainder being substantially titanium.

As taught in the cited Armstrong et al. patents, the reductant metal is generally present in excess of the stoichiometric amount needed to reduce the mixed halide vapor injected subsurface of the reductant metal. More particularly, when the reductant metal is present in the range of from about 20 to about 50 times the stoichiometric amount, which enables the entire steady state reaction to be maintained at or around 400°C, an advantageous and mostly preferred temperature. The exact temperature at which the steady state reaction is maintained depends, in part, upon the ratio of halide to reductant metal, as well as the individual vapors being reduced and the reductant metals used to reduce same. It is within the skill of the art to calculate the exact ratios required to provide a predetermined steady state operating temperature for the process producing any of the wide variety of ceramics or alloys made by the method and

apparatus of the present invention.

As previously stated, although the examples herein are discussed with respect to titanium or titanium alloys, a wide variety of alloys and ceramics may be made by the present invention and it is intended to cover in the claims appended hereto, all such alloy and ceramics particularly, but not exclusively, the nitride, boride or carbide ceramics. Representative alloys of the present invention are those which include one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si and most preferably one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A method of producing an alloy or ceramic by the exothermic subsurface reduction of a mixed halide vapor of the alloy or ceramic constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy or ceramic constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter introducing the equilibrium vapor into the liquid reductant metal to form an alloy or ceramic powder of the equilibrium vapor constituents in the preselected atomic ratio.
2. The method of claim 1, wherein the reductant metal is Na or Mg.
3. The method of claim 2, wherein the halide is a chloride.
4. The method of claim 3, wherein the alloy is principally Ti.
5. The method of claim 4, wherein the alloy is principally Ti and includes Al and V.
6. The method of claim 5, wherein the alloy is substantially 6% Al and 4% V with the remainder substantially Ti.
7. The method of claim 1, wherein the reductant metal is present in excess of the stoichiometric amount.
8. The method of claim 7, wherein the reductant metal is present in the range of from about 20 to about 50 times the stoichiometric amount.
9. The method of claim 7, wherein the reductant metal is present as a flowing stream.
10. The method of claim 1, wherein the vapor is introduced into the liquid metal by subsurface injection at greater than sonic velocity.
11. The method of claim 1, wherein the ceramic is one or more of a nitride or a carbide or a boride mixture thereof.
12. The method of claim 1, wherein the alloy includes one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.
13. The method of claim 12, wherein the alloy includes one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.
14. The method of claim 1, wherein at least some of the liquid halides are under pressure prior to forming the liquid mixture of halides.

15. A powder produced by the method of claim 1.

16. A solid produced from the powder of claim 15.

17. A method of producing an alloy by the exothermic subsurface reduction of a mixed halide vapor of the alloy constituents with liquid alkali or alkaline earth metal or mixtures thereof, comprising providing a liquid mixture of halides of the alloy constituents in a preselected atomic ratio, boiling the liquid until an equilibrium with the vapor is attained, and thereafter injecting the equilibrium vapor into the liquid reductant metal at greater than sonic velocity to form an alloy powder of the equilibrium vapor constituents in the preselected atomic ratio.

18. The method of claim 17, wherein the reductant metal is Na or Mg.

19. The method of claim 18, wherein the halide is a chloride.

20. The method of claim 19, wherein the alloy is principally Ti.

21. The method of claim 20, wherein the alloy is principally Ti and includes Al and V.

22. The method of claim 21, wherein the alloy is substantially 6% Al and 4% V with the remainder substantially Ti.

23. The method of claim 22, wherein the reductant metal is present in excess of the stoichiometric amount.

24. The method of claim 23, wherein the reductant metal is present in the range of from about 20 to about 50 times the stoichiometric amount.

25. The method of claim 24, wherein the reductant metal is present as a flowing stream.

26. The method of claim 17, wherein the reductant metal is Na and the halide is a chloride and the alloy includes one or more of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.

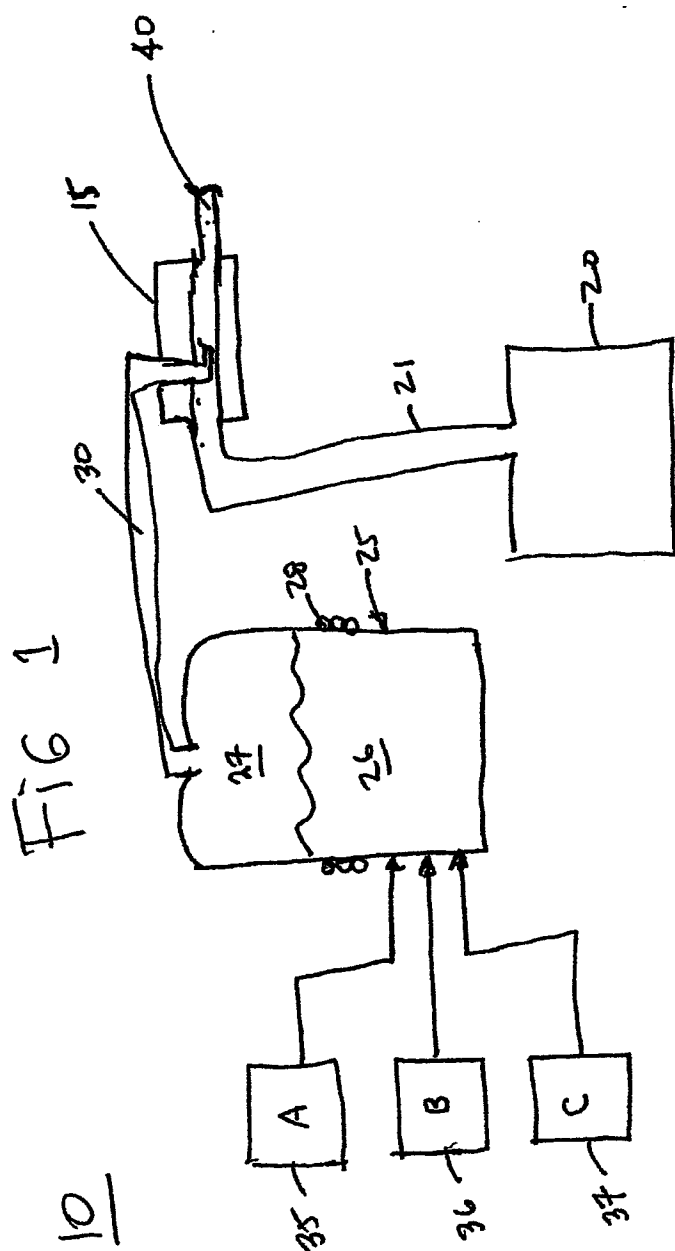
27. The method of claim 26, wherein the alloy includes one or more of Ti, Al, Ta, Zr, V, Nb, Mo, Ga, Re, or Si.

28. The method of claim 17, wherein one or more of the liquid halides is maintained under pressure.

29. A powder produced by the method of claim 17.

30. A solid produced from the powder of claim 29.

31. An apparatus for producing an alloy or ceramic by the subsurface reduction of a mixed halide vapor of the alloy or ceramic constituents with liquid alkali metal or alkaline earth metal or mixtures thereof, a container for storing each of the constituents in liquid form, a storage container for liquid alkali metal or alkaline earth metal or mixtures thereof, a boiler in communication with each of said containers for storing each of the constituents in liquid form, heating mechanism in heat exchange relationship with said boiler, a reactor in communication with said boiler and said storage container for the liquid metal, pumping mechanism for transferring a predetermined atomic ratio of each liquid constituent to said boiler, and pumping mechanism for transferring liquid metal from said storage container thereto to said reactor, whereby equilibrium vapor from said boiler infected subsurface of the liquid metal in said reactor produces an alloy or ceramic powder of the constituents in the predetermined atomic ratios.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27390

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B34/12 B22F9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 032 176 A (KAMETANI HIROSHI ET AL) 16 July 1991 (1991-07-16) abstract; figure 1 column 13, line 61 - column 14, line 9	1-13, 15-27, 29-31
X	US 5 958 106 A (ANDERSON RICHARD PAUL ET AL) 28 September 1999 (1999-09-28) cited in the application abstract column 3, line 28 - line 55	1-13, 15-27, 29-31
X	US 2002/005090 A1 (ANDERSON RICHARD PAUL ET AL) 17 January 2002 (2002-01-17) abstract paragraph '0019!	1-13, 15-27, 29-31

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

17 December 2003

Date of mailing of the international search report

15/01/2004

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Alvazzi Delfrate, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27390

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5032176	A	16-07-1991	JP 2024506 C	26-02-1996
			JP 2311316 A	26-12-1990
			JP 7047787 B	24-05-1995
			DE 4016502 A1	29-11-1990
			GB 2231883 A ,B	28-11-1990
US 5958106	A	28-09-1999	US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2002005090 A1	17-01-2002
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A ,B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
			RU 2152449 C1	10-07-2000
			WO 9604407 A1	15-02-1996
US 2002005090	A1	17-01-2002	US 5958106 A	28-09-1999
			US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A ,B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
			RU 2152449 C1	10-07-2000
			WO 9604407 A1	15-02-1996

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



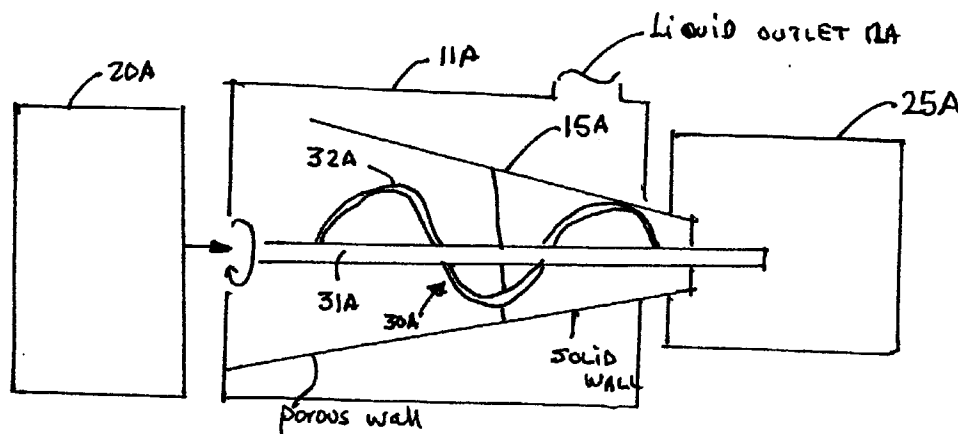
(43) International Publication Date
18 March 2004 (18.03.2004)

PCT

(10) International Publication Number
WO 2004/022798 A1

- (51) International Patent Classification⁷: **C22B 34/12**, 5/04, B30B 9/14, 9/12, B29C 47/08
- (74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar, 300 South Wacker Drive, #3000, Chicago, IL 60606 (US).
- (21) International Application Number:
PCT/US2003/027647
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date:
3 September 2003 (03.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/408,919 7 September 2002 (07.09.2002) US
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US]; 20634 W. Gaskin Drive, Lockport, IL 60441 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **ANDERSON, Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). **ARMSTRONG, Donn** [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).
- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: SCREW DEVICE FOR TRANSFER OF TI-CONTAINING REACTION SLURRY INTO A VACUUM VESSEL



(57) Abstract: A transfer mechanism between a first vessel containing a slurry of liquid and solids and a second vessel under vacuum. A housing is in communication with the first and second vessels and contains a screw in which the volume between adjacent screw threads and the housing diminishes between the first and the second vessels to form a plug sealing the second vessel from the first vessel. A method of forming the seal is also disclosed. The slurry typically may contain liquid alkali metal, titanium metal particles and halide salt particles such as obtained in the production of titanium metal by reduction of Ti halide with alkali metal.

WO 2004/022798 A1

FILTER EXTRACTION MECHANISM

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application U.S. Provisional Application Serial No. 60/408,919 Filed September 7, 2002.

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong process as described in 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. In the practice of the invention disclosed in the above referenced patents, there is produced in the reaction chamber a slurry consisting of excess reductant metal, salt particles produced and elemental material or alloy particles or powder produced. This slurry is thereafter treated by a variety of methods. However, all of the methods have in common the separation of excess liquid metal from the slurry and thereafter separating the remaining liquid metal and the produced salt from the desired product which is the elemental material or alloy. In the particular example disclosed in the three referenced patents, liquid sodium is used as a reductant for titanium tetrachloride to produce titanium powder.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a transfer mechanism and method for transferring a slurry of liquid and particles between two vessels or containers, at least one of which is under vacuum or inert atmosphere.

Yet another object of the present invention is to provide a transfer mechanism of the type set forth for the Armstrong Process in order to transfer slurry from an inerted vessel or container to a vacuum chamber for further processing wherein a seal is established in the transfer mechanism separating the vessels or containers.

Yet another object of the present invention is to provide a transfer mechanism between a first vessel containing a slurry of liquid and solids and a second vessel under vacuum, comprising a housing in communication with the first and the second vessels, a screw having a plurality of helical threads along a longitudinal shank within the housing for transferring material from the first vessel to the second vessel, the volume between adjacent screw threads and the housing diminishing between the first and the

second vessels, whereby slurry entering the housing from the first vessel has the solids therein concentrated as the slurry is transported by the screw toward the second vessel while liquid is expressed from the slurry as the solids are concentrated until the concentrated solids form a plug sealing the second vessel from the first vessel.

A further object of the invention is to provide a transfer mechanism between a first vessel containing a slurry of liquid alkali or alkaline earth metal or mixtures thereof and metal or alloy or ceramic particles and halide salt particles and a second vessel under vacuum, comprising a housing in communication with the first and the second vessels, a screw having a plurality of helical threads along a longitudinal shank within the housing for transferring material from the first vessel to the second vessel, the volume between adjacent screw threads and said housing diminishing between said first and the second vessels, whereby slurry entering the housing from the first vessel has the particles therein concentrated as the slurry is transported by the screw toward the second vessel while liquid metal is expressed from the slurry as the particles are concentrated until the concentrated particles form a plug sealing the second vessel from the first vessel.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantage of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic diagram showing the two vessels and an embodiment of the transfer mechanism therebetween;

FIG. 2 is a schematic of an alternate embodiment of the present invention; and

FIG. 3 is a schematic illustration of yet another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1 of the drawings, there is shown a transfer mechanism 10 which includes a double walled conduit including an outer conduit wall 11 having a liquid outlet 12 and end walls 13, the wall 11 being preferably but not necessarily cylindrical. Interior of the cylindrical wall 11 is an inner tube or conduit 15 having a portion 16 which is solid and a portion 17 which is apertured and may be a mesh of any suitable size. The inner tube or conduit 15 may either be cylindrical as illustrated in Fig. 1 or conical as will be explained, the inner conduit 15 has a discharge end 18 thereof which opens into a vacuum chamber 25 and has an inlet end 19 thereof which opens into a container or vessel 20 in communication with the reactor as illustrated in the Armstrong patents previously referenced and incorporated herein.

A feed screw 30 is positioned within the inner conduit 15 and includes a rotatable shank 31 having a conical thread 32 positioned on the shank 31 as is well known in the art. The thread 32 may have a constant or a variable pitch. The pitch is the distance between adjacent threads and the variable pitch may preferably be a progressive pitch in which the pitch decreases from the vessel 20 toward the container or vessel 25, for a purpose hereinafter described.

In the preferred but not limiting embodiment of the present invention, the transfer mechanism 10 is used in conjunction with a material made by the Armstrong Process. More particularly, for purposes of illustration only, the slurry discussed herein will be a combination of liquid sodium, sodium chloride particles and particles of titanium and/or a titanium alloy. As set forth in the Armstrong patents, a variety of metal and non-metal products may be made thereby and it is intended that the present invention not be limited to any particular product made by the Armstrong Process and certainly not limited to the preferred product described herein.

In any event, the vessel or container 20 preferably operated under an inert atmosphere or under vacuum has therein a slurry of the particles previously described and as the slurry enters the portion 19 of the inner conduit or tube 15 and the feed screw 30 is rotated as illustrated in the drawings by rotation of the shank 31, the slurry is moved along the feed screw from left to right as illustrated in Fig. 1. Because of the progressive pitch of the feed screw 30 in Fig. 1, that is the threads 32 thereof are closer together so that the pitch decreases from left to right, the material is concentrated as

it is moved from the container or vessel 20 to the container or vessel 25. Moreover, because the portion 17 of the conduit or tube 15 is apertured or porous, liquid sodium drains therethrough and passes out of the outlet 12 for further processing. Therefore, the slurry as it is transported from container or vessel 20 to container or vessel 25 becomes more concentrated as liquid is drained therefrom and the density increases as the pitch between the adjacent threads diminishes.

Another way to express what occurs is that the volume between adjacent threads and the wall of the cylinder or tube 16 diminishes as material is moved by the feed screw 30 from container or vessel 20 to container or vessel 25. By the time the slurry is concentrated and reaches the portion 16, the solid portion 16 of the inner tube or conduit 15, a seal is established between the vessel 25 and the vessel 20 which houses the slurry from the reactor. The formation of a seal by the transfer mechanism 10 is a critical aspect of the present invention because separation of liquid sodium and salt from the desired particles of the ceramic or metal alloy, as described in the Armstrong patents may include distillation in a vacuum chamber or a vessel 25 and the Armstrong reactor itself may be an inerted vessel such as with argon. Accordingly, it is important for a seal to be formed between the two containers or vessels in order to permit continuous operation between the two vessels without the necessity of shutting down one of the vessels during transfer or destroying the protective atmosphere in the vessel 20 or the vacuum in vessel 25.

Referring to Figs. 2 and 3, there are disclosed alternate embodiments of the invention. Again with the principle feature that the volume between adjacent screw threads and the container or housing in which the feed screw is positioned diminishes from vessel 20A to vessel 25A. As seen in Fig. 2, the transfer mechanism 10A has a housing 15A conical in shape and the screw 30 therein may or may not be a progressive pitch screw. The screw threads in the embodiment illustrated in Fig. 2 may not need to be closer together, that is the pitch need not be diminished in order to reduce the volume of the material between adjacent threads and the housing wall as the material is moved from left to right or from vessel 20A to vessel 25A. However, it may be advantageous to use both the conical shaped inner housing 15A with or without a progressive screw 30A depending on engineering considerations.

Referring to Fig. 3, there is shown another embodiment of the present invention in which the shank 31B of the screw 30B is conical in shape with the larger end of the cone being adjacent the vessel 25B and with the pitch between adjacent threads 32B being constant or diminishing. In either case, the volume of the area between adjacent threads and the inner container 15B diminishes as the material is moved from the vessel 20B to the vessel 25B.

Although the invention has been described with respect to an inerted vessel and a vacuum vessel, the invention includes movement and concentration of material from one container to another without compromising the environment of either container. The containers may be connected pipes or vessels, and the environments may be vacuums, inerted atmospheres or otherwise. Central to the invention is concentration of solids in a slurry to transport solids from one environment to another while forming a seal therebetween so as to isolate the environments from each other.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A transfer mechanism between a first vessel containing a slurry of liquid and solids and a second vessel under vacuum, comprising a housing in communication with said first and said second vessels, a screw having a plurality of helical threads along a longitudinal shank within said housing for transferring material from said first vessel to said second vessel, the volume between adjacent screw threads and said housing diminishing between said first and said second vessels, whereby slurry entering said housing from said first vessel has the solids therein concentrated as the slurry is transported by said screw toward said second vessel while liquid is expressed from the slurry as the solids are concentrated until the concentrated solids form a plug sealing said second vessel from said first vessel.
2. The transfer mechanism of claim 1, wherein said screw is a variable pitch screw.
3. The transfer mechanism of claim 1, wherein said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.
4. The transfer mechanism of claim 1, wherein said housing is generally cylindrical.
5. The transfer mechanism of claim 1, wherein said housing is conical with the smallest end being nearest said second vessel.
6. The transfer mechanism of claim 1, and further including in said transfer mechanism slurry of liquid metal and salt particles and particles of a ceramic or a metal or an alloy.
7. The transfer mechanism of claim 6, wherein said liquid metal is Na or Mg.
8. The transfer mechanism of claim 7, wherein said particles of a ceramic or a metal or an alloy are Ti or an alloy thereof.
9. The transfer mechanism of claim 1, wherein said housing is cylindrical and said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.
10. The transfer mechanism of claim 1, wherein said housing is conical with the smallest end being nearest said second vessel and said screw has threads of constant pitch.

11. The transfer mechanism of claim 1, wherein said shank has an increasing diameter toward said second vessel.

12. The transfer mechanism of claim 1, wherein at least a part of said housing in liquid communication with said first vessel has a plurality of apertures therein.

13. The transfer mechanism of claim 12, wherein the plurality of apertures is a mesh.

14. The transfer mechanism of claim 1, and further comprising an outlet in said housing for separating liquid flowing through said apertures from the slurry.

15. A transfer mechanism between a first vessel containing a slurry of liquid alkali or alkaline earth metal or mixtures thereof and metal or alloy or ceramic particles and halide salt particles and a second vessel under vacuum, comprising a housing in communication with said first and said second vessels, a screw having a plurality of helical threads along a longitudinal shank within said housing for transferring material from said first vessel to said second vessel, the volume between adjacent screw threads and said housing diminishing between said first and said second vessels, whereby slurry entering said housing from said first vessel has the particles therein concentrated as the slurry is transported by said screw toward said second vessel while liquid metal is expressed from the slurry as the particles are concentrated until the concentrated particles form a plug sealing said second vessel from said first vessel.

16. The transfer mechanism of claim 15, wherein said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

17. The transfer mechanism of claim 15, wherein said housing is generally cylindrical.

18. The transfer mechanism of claim 15, wherein said housing is conical with the smallest end being nearest said second vessel.

19. The transfer mechanism of claim 15, wherein said housing is cylindrical and said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

20. The transfer mechanism of claim 15, wherein said housing is conical with the smallest end being nearest said second vessel and said screw has threads of constant pitch.

21. The transfer mechanism of claim 20, wherein said shank has an increasing diameter toward said second vessel.

22. The transfer mechanism of claim 15, wherein at least a part of said housing in liquid communication with said first vessel has a plurality of apertures therein.

23. The transfer mechanism of claim 22, wherein the plurality of apertures is a mesh.

24. The transfer mechanism of claim 15, and further comprising an outlet in said housing for separating liquid flowing through said apertures from the slurry.

25. The transfer mechanism of claim 24, and further including a slurry of liquid Na, particles of NaCl and particles of Ti or an alloy thereof.

26. The transfer mechanism of claim 24, wherein a double wall housing is provided wherein the inner wall has a portion thereof apertured and a portion thereof solid and the outer wall has said outlet therein, said screw being positioned within said inner wall.

27. A method of concentrating and transferring a slurry from one container to another while sealing the containers, comprising providing communication between the containers, transporting slurry from one container toward another container while expressing liquid from the slurry thereby increasing the solids concentration thereof until a plug is formed between two containers while solids from the plug are transferred to the another container.

28. The method of claim 27, wherein one container is operated under an inert atmosphere.

29. The method of claim 27, wherein one container is operated under vacuum.

30. The method of claim 27, wherein the slurry contains liquid metal and metal particles.

31. The method of claim 30, wherein the slurry contains liquid alkali or alkaline earth metal.

32. The method of claim 27, wherein slurry contains liquid sodium metal and particles of Ti or an alloy thereof.

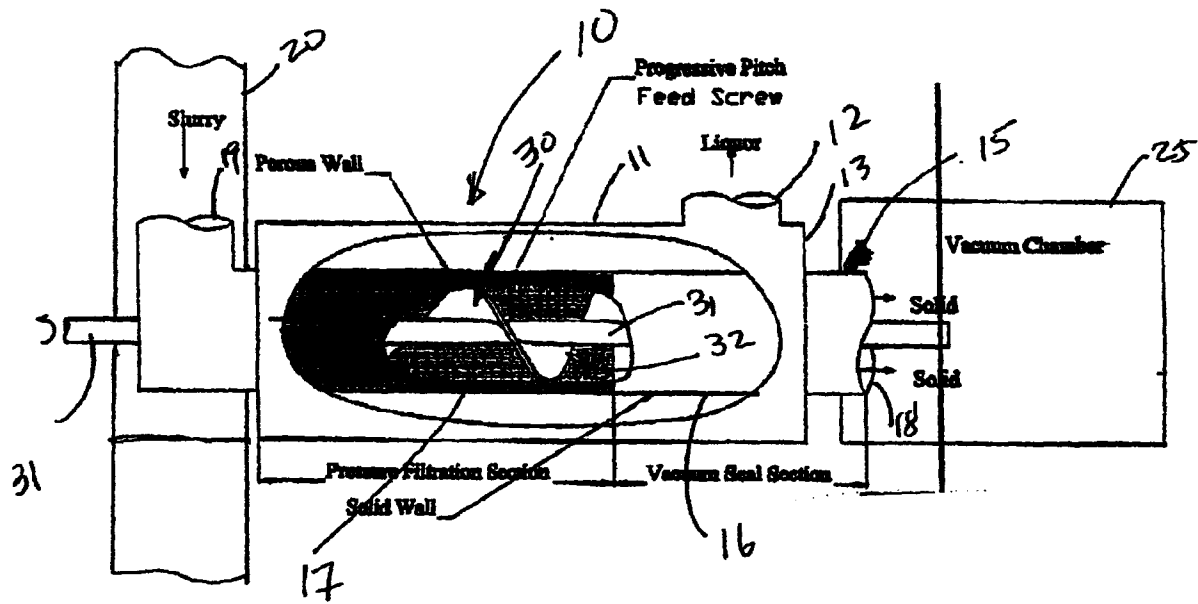


Fig 1

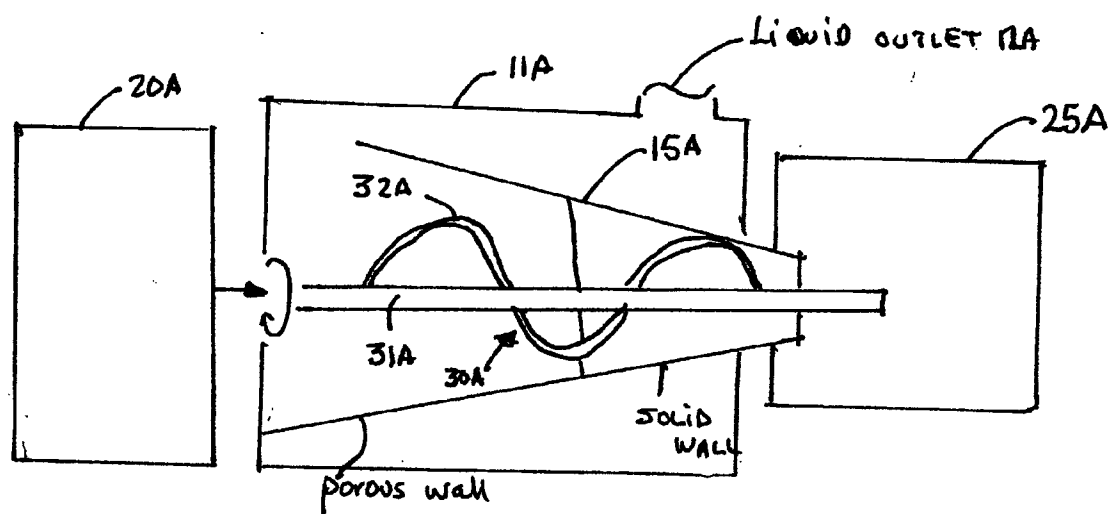


FIG. 2

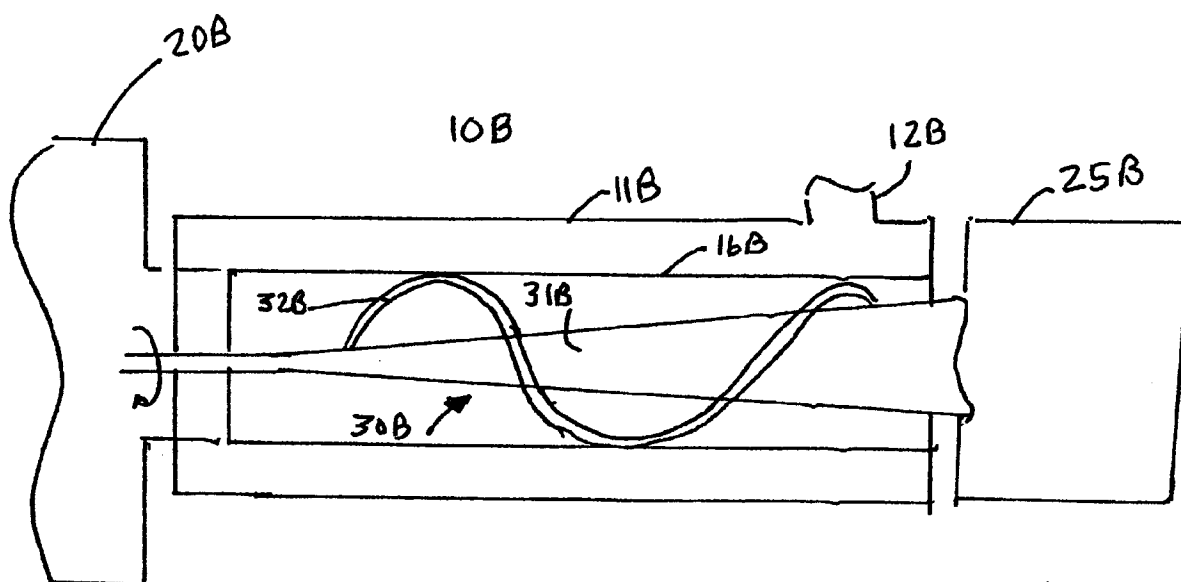


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27647

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B34/12 C22B5/04 B30B9/14 B30B9/12 B29C47/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B30B B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 839 120 A (BABA TOSHIO ET AL) 13 June 1989 (1989-06-13) column 2, line 57 -column 3, line 11; figure 1 ---	1-32
Y	US 3 919 087 A (BRUMAGIM IVAN S) 11 November 1975 (1975-11-11) abstract; figure 1 ---	1-5, 9-14, 16-24, 26,27
Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 130 (M-478), 14 May 1986 (1986-05-14) & JP 60 255300 A (YAMATO SANGYO KK), 16 December 1985 (1985-12-16) abstract --- -/--	1-32

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

9 January 2004

Date of mailing of the international search report

16/01/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bombeke, M

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27647

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) & JP 11 090692 A (CHIYODA CORP;ISHIGAKI:KK), 6 April 1999 (1999-04-06) abstract -----	1-32
Y	US 5 958 106 A (ANDERSON RICHARD PAUL ET AL) 28 September 1999 (1999-09-28) cited in the application column 5, line 66 -column 7, line 23; figures 1,3,4 -----	1,7,8, 15,25, 30-32

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/27647

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4839120	A	13-06-1989	JP 1864415 C	08-08-1994
			JP 5079001 B	01-11-1993
			JP 63207612 A	29-08-1988
			BE 1001673 A3	06-02-1990
			DE 3805569 A1	01-09-1988
US 3919087	A	11-11-1975	NONE	
JP 60255300	A	16-12-1985	NONE	
JP 11090692	A	06-04-1999	NONE	
US 5958106	A	28-09-1999	US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2002005090 A1	17-01-2002
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A ,B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
			RU 2152449 C1	10-07-2000
			WO 9604407 A1	15-02-1996

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
18 March 2004 (18.03.2004)

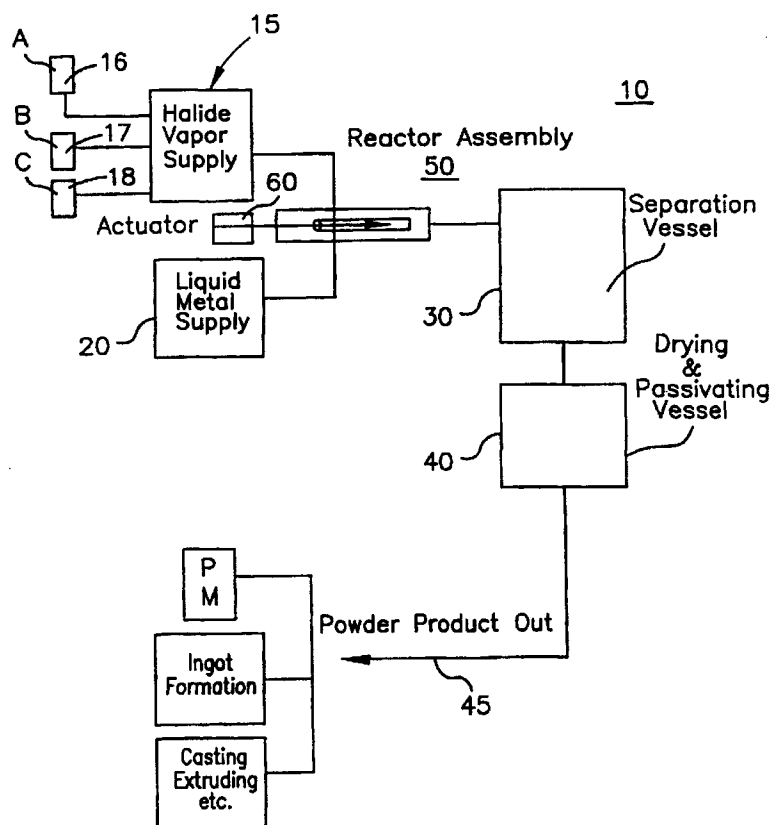
PCT

(10) International Publication Number
WO 2004/022799 A1

- (51) International Patent Classification⁷: **C22B 34/12**,
B22F 9/28
- (21) International Application Number:
PCT/US2003/027650
- (22) International Filing Date:
3 September 2003 (03.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/408,927 7 September 2002 (07.09.2002) US
- (71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **ANDERSON, Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). **ARMSTRONG, Donn** [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).
- (74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar, 300 South Wacker Drive, # 3000, Chicago, IL 60606 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),

[Continued on next page]

(54) Title: SAFETY MECHANISM



(57) Abstract: A safety mechanism used in the subsurface exothermic reduction of a halide vapor with a liquid reducing metal. A reactor for introducing halide vapor into the liquid metal causing an exothermic reaction forming a slurry of excess liquid metal and salt and a product powder. There is a source of halide vapor in fluid communication with said reactor and a source of liquid metal in fluid communication with the reactor. A porous plug is intermediate the source of the halide vapor and the source of liquid metal preventing liquid metal from infiltrating the source of halide vapor by forming a seal in said porous plug upon contact with liquid metal.



Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— with amended claims and statement

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— with international search report

SAFETY MECHANISM

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application U.S. Provisional Application Serial No. 60/408,927 filed September 7, 2002.

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong process as described in U.S. patents 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. In the method described in the above-referenced patents, the halide vapor is introduced into the reductant liquid metal at a flow velocity which is equal to or greater than sonic in order to preclude the backup of liquid metal into the halide vapor supply. Such a backup could be catastrophic. This invention relates to an additional safety measure in the use of a porous plug such as porous metal mesh or sintered metal powder in the inlet line between the nozzle where the halide vapor flows into the liquid metal and the source of the halide vapor. A porous plug as previously described which has a material therein which swells upon contact with the reductant metal (sodium) would, upon contact with the liquid metal reductant (sodium), react and swell forming a seal in the line preventing any additional reductant (sodium) from being sucked into the halide supply.

Accordingly, this invention relates to a porous plug in the inlet line between the titanium tetrachloride boiler and the injection point 23 as illustrated in Fig. 2 of the '106 patent. The porous plug seals either with sodium chloride which solidifies in the plug, or the plug may have a material such as graphite which reacts with liquid reductant (sodium) to swell in the plug and form a seal or a combination of both. This invention provides an important safety feature since check valves are notoriously unreliable and because of the possibility that a catastrophic explosion could occur should the halide vapor boiler fail and a vacuum be created, thereby sucking sodium into the halide boiler and/or the halide supply.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a safety device in a system for practicing the Armstrong Process.

Still another object of the invention is to provide a simplified, easy insert into the line between the halide vapor boiler and the reactor which precludes the back-up of liquid metal into the halide boiler.

Yet a further object of the invention is to provide a system for producing a powder by the subsurface exothermic reduction of a halide vapor with a liquid alkali metal or alkaline earth metal or mixtures thereof, comprising a reactor for introducing halide vapor into the liquid metal causing an exothermic reaction forming a slurry of excess liquid metal and salt and a product powder, a source of halide vapor in fluid communication with said reactor, a source of liquid metal in fluid communication with the reactor, and a porous plug intermediate the source of the halide vapor and the source of liquid metal preventing liquid metal from infiltrating the source of halide vapor by forming a seal in said porous plug upon contact with liquid metal.

Yet another object of the invention is to provide a powder produced by the system previously described having the additional safety feature herein described.

A final object of the present invention is to provide a solid product made from a powder produced by the use of the system disclosed herein.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of a system for practicing the present invention; and.

FIGURE 2 is a schematic representation of a needle valve assembly useful in the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to Figure 1, there is shown a system 10 for the practice of the present invention including a supply of halide vapor 15 which in turn is in fluid communication with a plurality of liquid halide or solid halide materials, shown for purposes of illustration only as supplies 16, 17 and 18 for halide liquids or solids A, B and C respectively. The system 10 further includes a supply of liquid metal 20 which may be any alkali or alkaline earth metal or various mixtures thereof, sodium and magnesium being preferred with sodium being mostly preferred.

Similarly, with respect to the halide vapor supply 15, chlorides are preferred and more specifically, one or more of the chlorides of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re and Si.

There is further provided a separation vessel 30 in fluid communication with a reactor assembly 50, as will be described, and in fluid communication with a drying and passivating vessel 40. A powder product outlet 45 is in communication with the drying and passivating vessel 40, as will be described, the powder being either the final product or an intermediate product of the system and process of the invention.

The present invention and system 10 includes the reactor assembly 50, as seen in Fig. 2, which has an outer cylinder 51 having an exit portion 52 which may be of reduced diameter or of the same diameter as the remainder of the outer cylinder or conduit 51, as preferred.

The reactor assembly 50 serves to receive the halide vapor of the metal or ceramic to be produced and the liquid reducing metal and to introduce the halide vapor in a controlled fashion but at not less than sonic velocity subsurface of the reducing metal or into a stream of the reducing metal so that the temperature of the reaction is controlled, in part, by the excess of the reducing metal, all is taught in the above-referenced patents.

The reactor assembly 50 has one-half of a sealing ring 54 on the exit nozzle portion 52 to sealing engage another sealing ring (not shown) located in the vessel into which the exit portion 52 is positioned. The outer cylinder 51 also has a inlet nozzle portion 56 which terminates in an end 57. An actuator 60, either pneumatic or otherwise, as is known in the art, is in communication with the reactor assembly 50 and particularly the outer cylinder 51 as will be explained. The outer cylinder 51 also has

a pressure tap 62 which may be for the introduction of an inert gas such as argon or to vent the assembly 50, if required, or to monitor the pressure within the outer cylinder 51. Also provided is a reducing metal inlet 64, in the illustration a sodium inlet. Both the pressure tap 62 and the reducing metal inlet 64 extend through the outer cylinder 51 and are sealed thereto.

A sealing ring is made up of mating halves 66 and 67 intermediate the actuator 60 and the exit nozzle portion 52 of the reactor assembly 50. A halide inlet tap 69 extends into the inlet nozzle portion 56 of the outer cylinder 51 and is sealed downstream of the inlet 69 by means of the sealing rings 66, 67 and is in fluid communication with a housing 79 which may be generally cylindrical in shape and extends from the sealing half ring 66 through the outer cylinder 51 and terminates at an end 81 having a valve seat therein.

A needle valve 75 includes an elongated cylindrical shaft portion 76 having a conical shape valve portion 77 and another end 78 in communication with the actuator 60. The halide inlet 69 introduces halide vapor into the chamber formed by the inlet nozzle portion 56 of the outer cylinder 51 and enters the housing 79 by virtue of the communication between the end of the housing 79 and the sealing rings 66, 67. The sodium entering through sodium inlet 64 is on the outside of the housing 79 and completely fills the outer cylinder 51 and flows axially of the outer cylinder. The longitudinal axial movement of the needle valve 75 by means of the actuator 60 causes the conical end portion 77 to seat within a valve seat in the end 81 of the housing 79, it being apparent to those of ordinary skill in the art that the diameter of the valve seat in the end 81 must be smaller than the diameter of the shaft portion 76 of the needle valve 75. Valve seats 81 between 1/8 and 3/8 inch have been used with the appropriate change in shaft portion 76.

It is important that no sodium be able to back up through the valve seat in the end 81 into the halide vapor supply. That necessity is accomplished by using not less than sonic flow of the halide through reactor assembly 50 as taught in the referenced patents and is insured by a porous plug 70 in the line between the vapor supply or boiler 15 and the needle valve 50. As regards the actuator 60, it may be operated to move the shaft portion 76 axially of outer cylinder 51 to the right in Fig. 2, so that the conical portion 77 of the needle valve 75 begins to seat within the valve seat in the end

81, the amount or volume of halide vapor, such as titanium tetrachloride, introduced into the sodium or reducing metal inside the outer cylinder 51 is reduced or controlled permitting the operators of the system to vary the time and rate of delivery of the halide vapor. Another advantage of the needle valve 75 is that when the needle valve 75 is fully seated within the valve seat in the end 81, a vacuum may be drawn upstream of the nozzle or reactor assembly 50 before startup of the production of the metal by the exothermic reaction of the halide with the reducing metal.

Turning now to the porous plug 70, it may be any suitable porous or perforated metal, such as but not limited to stainless steel. The plug 70 may be apertured or it may be a mesh, the purpose being if a catastrophic failure in protection occurred, as liquid metal moved toward the halide supply or boiler 15, a reaction would occur in the plug 70 forming salt particles which would seal the vapor supply or boiler 15 from the liquid metal supply 20. In addition, the plug 70, not being heated, should form a heat sink cooling the reactants sufficiently to solidify the formed salt. Cooling fins (not shown) or other cooling mechanism, well known in the art, may be useful in conjunction with plug 70 to ensure no liquid metal reaches the vapor boiler or supply 15. The size of the plug 70 is not shown to scale and is within the skill of the art to determine the diameter and length required to prevent back-up of liquid metal into the vapor supply 15. Another aspect of the invention is to contact the interior of the plug 70 with a material which reacts with the liquid metal, but not the halide vapor, that swells and seals the plug. For sodium metal, graphite is acceptable as it swells upon contact with liquid sodium and would form an effective seal. Other materials are within the skill of the art to identify and employ.

It is seen that the powder product 45 discharged from the drying and passivating vessel 40 may be used as a product in and of itself or may be used in powder metallurgy to produce product or ingot or other means by which solid product is formed which also includes casting, extruding or other methods. Any solid product or object made from the powder 45 produced by the inventive system 10 is within the purview of the present invention.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A system for producing a powder by the subsurface exothermic reduction of a halide vapor with a liquid alkali metal or alkaline earth metal or mixtures thereof, comprising a reactor for introducing halide vapor into the liquid metal causing an exothermic reaction forming a slurry of excess liquid metal and salt and a product powder, a source of halide vapor in fluid communication with said reactor, a source of liquid metal in fluid communication with the reactor, and a porous plug intermediate the source of the halide vapor and the source of liquid metal preventing liquid metal from infiltrating the source of halide vapor by forming a seal in said porous plug upon contact with liquid metal.

2. The system of claim 1, wherein said plug is porous metal.

3. The system of claim 1, wherein said plug is metal mesh.

4. The system of claim 1, wherein said plug is sintered metal powder.

5. The system of claim 1, wherein said plug contains a substance reactive with said liquid metal sealing said plug upon contact by said liquid metal.

6. The system of claim 5, wherein said plug contains graphite.

7. The system of claim 1, wherein said source of liquid metal is Na or Mg.

8. The system of claim 1, wherein said source of liquid metal is Na.

9. The system of claim 1, wherein said source of halide is a chloride.

10. The system of claim 1, wherein said source of halide is a mixture of chlorides.

11. The system of claim 1, wherein said source of halide includes one or more of the chlorides of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re and Si.

12. The system of claim 11, wherein said liquid metal is Na.

13. A powder produced by the operation of the system of claim 1.

14. A solid product made from the powder of claim 13.

AMENDED CLAIMS

Received by the International Bureau 13 February 2004 (13.02.04) ;
Original claims 1 replaced by amended claims 1.

WHAT IS CLAIMED IS:

1. A system for producing a powder by the subsurface exothermic reduction of a halide vapor with a liquid alkali metal or alkaline earth metal or mixtures thereof, comprising a reactor for introducing halide vapor into the liquid metal causing an exothermic reaction forming a slurry of excess liquid metal and salt and a product powder, a source of halide vapor in fluid communication with said reactor, a source of liquid metal in fluid communication with the reactor, and a porous plug intermediate the source of the halide vapor and the source of liquid metal preventing liquid metal from infiltrating the source of halide vapor by forming a seal in said porous plug upon contact with liquid metal.

2. The system of claim 1, wherein said plug is porous metal.

3. The system of claim 1, wherein said plug is metal mesh.

4. The system of claim 1, wherein said plug is sintered metal powder.

5. The system of claim 1, wherein said plug contains a substance reactive with said liquid metal sealing said plug upon contact by said liquid metal.

6. The system of claim 5, wherein said plug contains graphite.

7. The system of claim 1, wherein said source of liquid metal is Na or Mg.

8. The system of claim 1, wherein said source of liquid metal is Na.

9. The system of claim 1, wherein said source of halide is a chloride.

10. The system of claim 1, wherein said source of halide is a mixture of chlorides.

11. The system of claim 1, wherein said source of halide includes one or more of the chlorides of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re and Si.

12. The system of claim 11, wherein said liquid metal is Na.

13. A powder produced by the operation of the system of claim 1.

STATEMENT OF ARTICLE 19

Claim 1 is amended to correct a typographical error.

1/2

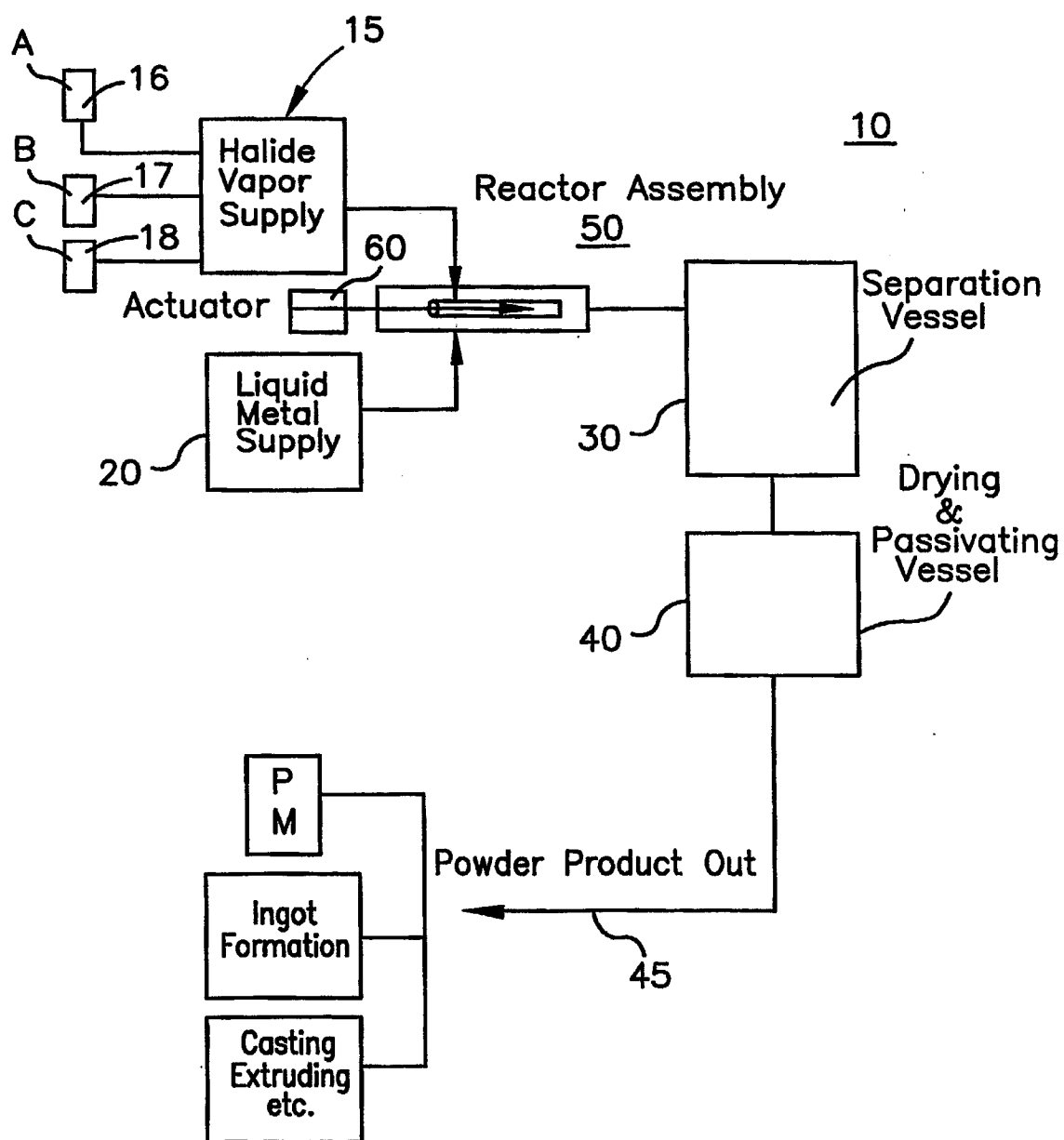


FIG. 1

2/2

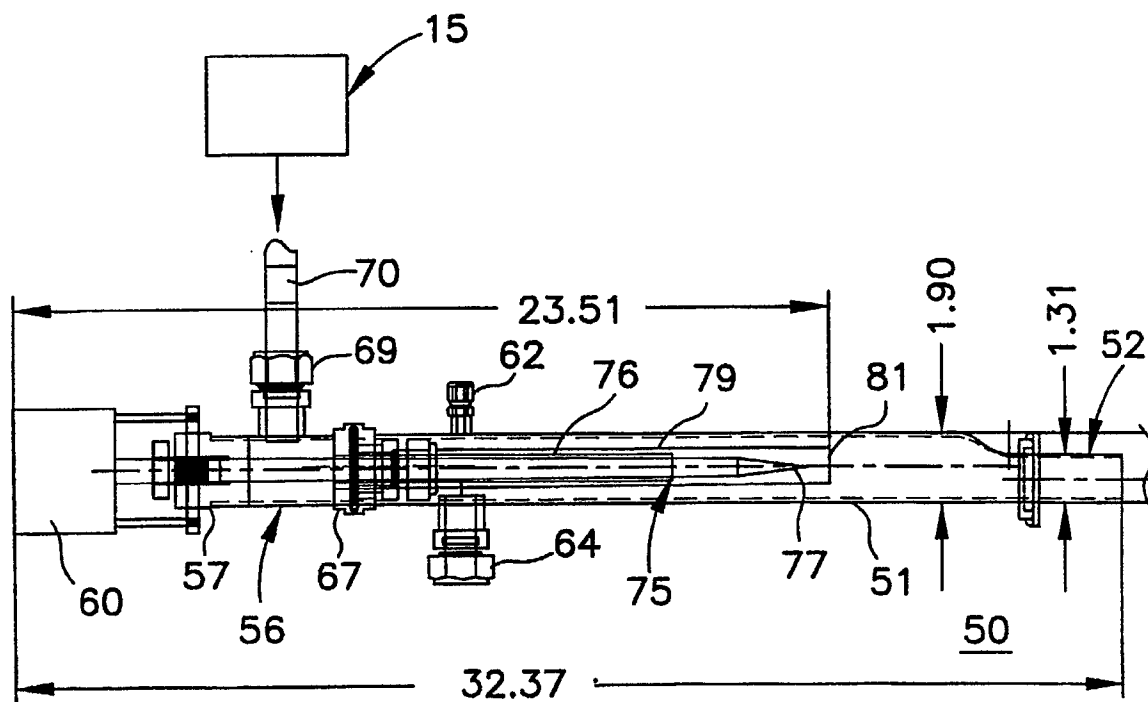


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US 03/27650

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B34/12 B22F9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 958 106 A (ANDERSON RICHARD PAUL ET AL) 28 September 1999 (1999-09-28)	1
X	cited in the application abstract	13,14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

15 December 2003

Date of mailing of the international search report

15/01/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Alvazzi Delfrate, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 03/27650

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5958106	A	28-09-1999	US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2002005090 A1	17-01-2002
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A ,B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
			RU 2152449 C1	10-07-2000
			WO 9604407 A1	15-02-1996



Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

— before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

PROCESS FOR SEPARATING TI FROM A TI SLURRY

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application serial No. 60/408,932, filed September 7, 2002, U.S. Provisional Application Serial No. 60/408,925, filed September 7, 2002 and U.S. Provisional Application Serial No. 60/408,933, filed September 7, 2002

BACKGROUND OF THE INVENTION

This invention relates to the separation of unwanted constituents from a slurry produced during operation of the Armstrong Process and method to produce a product as disclosed in U.S. patent nos. 5,779,761, 5,958,106 and 6,409,797 patents, the disclosures of which are herein incorporated by reference. As indicated in the above-identified and incorporated patents, the continuous process there disclosed, produces, for instance, titanium or a titanium alloy by the reduction of titanium tetrachloride with excess sodium. The product stream that exits the reactor is a slurry of liquid metal, salt particles or powder and titanium metal or metal alloy as particulates or powder. It should be understood that this invention relates to any material which can be made according to the Armstrong Process. When the slurry produced by the Armstrong Process is filtered, a gel or gel-like material is formed of the metal powder or particulates, the salt powder or particulates and the excess liquid reducing metal. This slurry has to be treated to separate the unwanted constituents, such as excess liquid metal, salt particulates from the desired end product which is the metal particulates or powder.

SUMMARY OF THE INVENTION

In developing the Armstrong Process with respect to titanium and its alloys, it has been found that the method of producing the slurry above referenced is very rapid and separation of the product from the slurry is the most difficult aspect in engineering of the continuous process. The description will be in terms of the exothermic reduction of titanium tetrachloride with sodium to produce titanium particles, sodium chloride particles and excess sodium; however, this is not to be

construed as a limitation of the invention but for convenience, only.

Accordingly, it is an object of the present invention to provide a method for separating metal powder or particulates from a slurry of liquid metal and metal powder or particulates and salt powder or particulates.

Yet another object of the present invention is to provide a method of separating metal particulates from a slurry of the type set forth in which one of the unwanted constituents is used to separate both constituents from the slurry.

A still further object of the present invention is to provide a method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising concentrating the metal and salt particulates by removing at least some of the liquid metal, passing the liquid metal or a liquid of the original salt constituent or a mixture thereof at a temperature greater than the melting point of the original salt constituent or mixture thereof through the concentrated metal and the particulates to further concentrate the metal particulates, and thereafter separating the metal particulates from the remaining original constituents or a mixture of the salt constituent.

A final object of the present invention is to provide a method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising introducing the slurry of original constituents into a vessel having a liquid salt therein wherein layers form due to density differences with the liquid metal being the lightest and the metal particulates being the heaviest increasing the concentration of the metal particulates toward the bottom of the vessel, removing liquid metal from the vessel, separating the concentrated metal particulates with some liquid salt from the vessel, filtering the salt from the metal particulates, and thereafter cooling and water washing the salt from the metal particulates.

Additional advantage, objects and novel feature of the invention will become apparent to those skilled in the art upon examination of the following and by practice of the invention.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and

particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic illustration of a first embodiment of the invention;

Fig. 2 is a schematic illustration of another embodiment of the present invention; and

Fig. 3 is a schematic illustration of another embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings and more particularly to Fig. 1, there is shown a separation system 10 in which a vessel 15 has a generally cylindrical portion 16 with a dome shaped top 17 and a frustoconical shaped bottom 18 and exit pipe 19 extending from the bottom of the vessel 15. A reactor 20 of the type disclosed in the above-referenced patents has a outer liquid metal or sodium tube 21 and an inner halide vapor or titanium tetrachloride tube 22. A liquid metal or sodium supply tank 25 feeds sodium to the sodium or other liquid metal to the reactor 20 and a halide boiler 26 feeds the appropriate halide vapor to the reactor 20, all as previously described.

Internally of the vessel 15 is a downwardly sloping baffle 28 having a distal end 28a extending at a more acute angle and generally opposite to a sodium or liquid metal outlet 29. The liquid metal outlet 29 is in fluid communication with a metal or sodium pump 31 which leads to a heat exchanger 33 having a fluid inlet 34 and a fluid outlet 35. A liquid metal make-up line 37 is in communication with the supply tank or reservoir 25. A vent line 38 is provided in the tank or reservoir 25, as is well known in the engineering art.

A valve 40 with an actuator 41 is positioned in the exit 19 of the vessel 15 which is in communication with two exit lines 42 and 43, each of which being provided with a valve such as a valve 44 illustrated in line 42.

A filter assembly 45 includes a container 46 and a sloping filtered plate 47 for a purpose hereinafter set forth. A passivating gas inlet 50 has a valve 51 intermediate the source of passivating gas (not shown) and the container 46. A vacuum drying line 52 exits the container 46 and is provided with a valve 53. A slurry outlet line 56 at the bottom of the container 46 is provided with a valve 57 and a salt outlet line 61 is provided with a valve 62. Finally, a water wash inlet pipe 66 is provided with a valve 57.

The separation system 10 operates in following manner wherein material such as a metal or metal alloy is produced in the reactor 20 by the method previously described in the aforementioned and incorporated Armstrong patents. By way of illustration only, titanium or a titanium alloy may be made by the reduction of titanium tetrachloride vapor or a plurality of halide vapors for an alloy by an alkali or alkaline earth metal such as sodium or magnesium. Alloys are easily made with the Armstrong Process by mixing the halide vapors in the appropriate quantities and reducing them in the exact same manner as hereinbefore described. In any event, using a large excess of the reducing metal to control the reaction produces a slurry of excess reducing metal, such as sodium, the metal particulates such as titanium and another reaction product such as salt particles, sodium chloride. The slurry leaving the reactor 20 may be at a variety of temperatures controlled, in one instance, by the amount of excess reducing metal present.

In an actual example, the slurry may typically have up to about 10% by weight particulates, and the particulates may be salt having diameters on average of from about 10 to about 50 microns and titanium having diameters on average in the range of from about 0.1 micron to about 500 microns, the titanium particulates or powder may be more likely to be in the range of from about 1-10 microns and the agglomerated ligaments (lumps) of the titanium in the range of between about 50 and about 1000 microns. This combination of liquid metal, salt particulates and titanium particulates leave the nozzle 20 and enter the vessel 15. The salt in the

vessel 15 is indicated to be at a level of which may be arbitrarily chosen so long as it is below the sodium outlet 29. The salt may be the reaction product salt, for instance sodium chloride, or a salt mixture which has a melting point lower than the reaction product salt. Although the salt may be as stated any salt, preferably the salt is the product of reaction or a mixture thereof, for instance an eutectic such as the calcium chloride- sodium chloride eutectic which melts at about 600°C.

The entire system 10 then may be operated at a lower temperature. For instance, sodium chloride melts at about 850°C. so if the salt in the vessel 15 is sodium chloride, then the vessel 15 must be operated above the melting point thereof, but as the eutectic melts at 600°C, this reduces the operating temperature. In any event, irrespective of what salt is present at the level 30 in the vessel 15, the liquid metal will float due to density differences and be extracted through the outlet 29 by means of the sodium or liquid metal pump 31. A heat exchanger 33 having suitable inlet and outlet lines 34, 35 serves to reduce the temperature of the sodium out from the 600° in the vessel 15 (by way of example only) so that the recycled sodium enters the reactor 20 at a preselected temperature (for instance about 400°C). The baffle 28 and 28a prevents particulates entering the vessel 15 from the reactor 20 from being sucked into the sodium outlet 29.

As particulates settle in the lower portion 18 of the vessel 15, the particulate concentration is increased due to the removal of sodium through the line 29. Upon actuation of the valve 40, concentrated slurry will drain through the outlet or exit 19 through line 42 into the filter assembly 45. In the filter assembly 45, which is maintained by temperatures sufficient to keep the molten salt in a liquid phase, metal particles collect on the filter plate 37 while salt passing through the filter plate exits through line 61 to be returned, for instance, to an electrolytic cell (not shown). The valve 62 opens the line 61 to permit the salt to drain while valve 57 is closed to prevent material from exiting the filter assembly 45. After a sufficient filter cake has been built up, the valve 62 is closed, the valve 44 is closed and the vacuum drying line 53 is opened after the filter cake has cooled to less than about 100 °C so that the passivating gas which may be argon and a small percentage of oxygen may be introduced into the container 46 by actuation of the valve 51. After the filter cake

which may be principally titanium powder with some salt is passivated, then the valve 51 is closed and the water wash valve 67 opened thereby allowing water to enter into the container 46 which both dissolves salt and moves the filter cake through line 56 to a finish wash and classification, it being understood that valve 67 will be opened prior to the water wash. The salt coming out of the filter assembly 45 through line 61 can be recirculated to the vessel 15 as indicated by the line 61a.

As seen therefore, the separation system 10 depends on the difference in gravity between the unwanted liquid metal constituent of the slurry and the salt and metal particulates produced during the reaction of the dried vapor and the reducing metal. Although this separation system 10 is a batch system, it can be rapidly cycled from one filter assembly 45 to other filter assemblies as needed through a simple valve distribution system, as is well known in the art.

Although the above example was illustrated with sodium and titanium tetrachloride, it should be understood that any material made by the Armstrong Process may be separated in the aforesaid manner.

Figure 2 shows an alternate embodiment separation system 80 in which a vessel 85 is similar to the vessel 15 and has a cylindrical portion 86, a dome top 87 and a frustoconical bottom 88 having an exit 89 extending therefrom. A reactor 90 of the same type as hereinbefore described is in communication with the vessel 85 and has a halide inlet 91 and a reducing metal inlet 92. A slurry outlet 93 which is in communication with the top 87 of the vessel 85. The filter 95 is any suitable filter, well known in the art, but preferably, for purposes of illustration only, is a "wedge screen filter" of a size to pass up to 125 micron particles. The material that flows through the filter 95 exits the vessel 85 through an output line 96 and flows into a gravity separator 97. The gravity separator 97 is frustoconical in shape and has an outlet 99 through which the heavier of the materials flows, in this particular case sodium chloride. An outlet 98 takes the lighter of the material, in this case sodium and recycles same through appropriate filters and other mechanisms, not shown, to the reactor 90. In this embodiment, the vessel 85 is maintained at an elevated temperature of about 850°C with either internal or external heaters, as is well known in the art, in order that the salt in this case, sodium chloride, is liquid or molten. The

molten sodium in large excess displaces the sodium chloride around the particulates and therefore the sodium and the salt flows through the filter plate 95 into the gravity separator 97 and is recycled as previously described. After a suitable filter cake is built up on the filter plate 95, the valves are closed and the filter cake is thereafter removed for further processing. The advantage of the embodiment disclosed herein is that one of the unwanted constituents, that is the sodium liquid metal is used to displace the other unwanted constituent which in this case is the molten salt. Suitable heat exchangers are required to reduce the temperature of the exiting sodium in line 98 before it is recycled and to heat and maintain the temperature of the salt in the molten state in both the vessel 85 and in the vessel 97.

Referring now to Figure 3, there is another embodiment of the present invention illustrated as the separation system 100. The separation system 100 is provided with similar equipment as illustrated in embodiments 10 and 80. In the system 100, there is a vessel 105 having a cylindrical portion 106, a dome shaped top portion 107 and a frustoconical shaped bottom portion 108 having an exit 109 at the bottom thereof. A reactor 110 of the type described in the previously described for practicing the Armstrong process has, as for example only, a titanium tetrachloride inlet 111 and a sodium inlet 112 which serves to produce the reaction previously described with the outlet 113 carrying the slurry produced from the reaction.

A gravity separator 117 is frustoconical in shape and has an outlet 118 for the lighter weight liquid metal such as sodium and a bottom outlet 119 through which the heavier unwanted constituent, in the present case sodium chloride, exits. Suitable valves are provided between the exit line 116 and the gravity separator 117 as indicated by the valve 121 and a valve 122 is in the exit line 116 between the vessel 105 and the sodium inlet 112. Another valve 123 is intermediate the vessel 105 and the sodium chloride outlet from the gravity separator 117 and finally a valve 124 is intermediate the reactor 110 and the vessel 105.

In the present system 100, the filter plate 115 collects the metal particulates as the salt which is molten and at a suitable temperature such as greater than the melting points, such as 850°C. for sodium chloride flows through the filter plate 115

carrying with it excess molten sodium which is displaced from the filter cake as it builds on the filter 115. The combination of liquid sodium and liquid salt flows out of the vessel 105. Closing valve 122 and opening the valve 121 results in the material being moved by a suitable pump (not shown) to the gravity separator 117. In the gravity separator 117, the liquid metal sodium floats and the liquid salt forms the heavier layer at the bottom of the separator 117 and is separated as indicated with the sodium being drawn off at the top of the separator through line 118 to be recycled (after cooling if required) to the sodium inlet to the reactor 110. The salt is recycled through valve 123 to the vessel 105. The reactor 110 can be isolated from the system by the valve 124 so that after a predetermined amount of time, the reactor can be disconnected from the system and shunted to a different separation module while liquid salt is used to displace liquid sodium present in the vessel 105 and in the titanium particulates forming the cake on the filter 115.

Although the separation systems disclosed herein are batch operations, the valving is such that continuous separations can occur while the reactor is running. A simple system of two or more of the separation systems 10, 80 or 100 permits a reactor continuously to produce the product of the Armstrong reaction.

Although described herein with reference to titanium and sodium, any alkali metal or alkaline earth metal or various combinations thereof may be used as the reductant metal. Any halide may be useful or any combinations of halides may be useful as the vapor which is injected into the liquid metal to cause the exothermic reaction to occur. For reasons of economics, sodium or magnesium are preferred with sodium being mostly preferred. For other reasons, titanium tetrachloride along with the chlorides of vanadium and aluminum are also preferred in order to make titanium powder or various titanium alloys, the titanium 6:4 alloy being the most preferred titanium alloy presently in use. The 6:4 titanium alloy is 6% aluminum and 4% vanadium with the remainder titanium, as is well known in the art.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WE CLAIM:

1. A method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising concentrating the metal and salt particulates by removing at least some of the liquid metal, passing the liquid metal or a liquid of the original salt constituent or a mixture thereof at a temperature greater than the melting point of the original salt constituent or mixture thereof through the concentrated metal and salt particulates to further concentrate the metal particulates, and thereafter separating the metal particulates from the remaining original constituents or a mixture of the salt constituent.

2. The method of claim 1, wherein a gel is formed when at least some of the liquid metal is removed.

3. The method of claim 1, wherein liquid metal at a temperature at or above the melting point of the original salt constituent or mixture thereof and contacts the concentrated metal and salt particulates to displace salt particulates and further concentrate the metal particulates.

4. The method of claim 1, wherein a liquid of the original salt constituent contacts the concentrated metal and salt particulates to dissolve or displace salt particulates further to concentrate the metal particulates.

5. The method of claim 1, wherein a liquid mixture of the original salt constituent contacts the concentrated metal and salt particulates to dissolve or displace salt particulates further to concentrate the metal particulates.

6. The method of claim 1, wherein the original constituent of liquid metal is an alkali or an alkaline earth metal or mixtures thereof.

7. The method of claim 1, wherein the liquid original salt constituent or mixture thereof is maintained at a temperature below the sintering temperature of the metal particulates during the further concentration thereof.

8. The method of claim 7, wherein the mixture of the original salt constituent is the eutectic or substantially the eutectic of NaCl and CaCl₂.

9. The method of claim 1, wherein the metal particulates are a Ti or Ti alloy.

10. The method of claim 9, wherein the Ti alloy is 6% Al, 4% V and the remainder substantially Ti.
11. The method of claim 1, wherein the liquid metal is sodium heated to temperature greater than about 600 C.
12. The method of claim 11, wherein the sodium is heated to a temperature greater than about 800 C.
13. The method of claim 1, wherein a liquid of the original salt or a mixture thereof is heated to a temperature greater than about 600 C.
14. The method of claim 1, wherein the metal particulates are Ti or a Ti alloy and the liquid metal is Na and the salt particulates are NaCl.
15. The method of claim 14, wherein the metal particulates are a Ti alloy of 6% Al and 4% V and the remainder being substantially Ti.
16. A method of separating metal particulates from a slurry of original constituents of liquid metal and metal particulates and salt particulates, comprising introducing the slurry of original constituents into a vessel having a liquid salt therein wherein layers form due to density differences with the liquid metal being the lightest and the metal particulates being the heaviest increasing the concentration of the metal particulates toward the bottom of the vessel, removing liquid metal from the vessel, separating the concentrated metal particulates with some liquid salt from the vessel, filtering the salt from the metal particulates, and thereafter cooling and water washing the salt from the metal particulates.
17. The method of claim 16, wherein the liquid salt is substantially the same as the salt particulates.
18. The method of claim 16, wherein the liquid salt is a mixture of the salt particulates.
19. The method of claim 16, wherein the liquid salt is an eutectic or substantially the eutectic of the salt particulates.
20. The method of claim 19, wherein the eutectic contains Na and CaCl_2 .
21. The method of claim 16, wherein the liquid salt is maintained at a temperature of less than about 800 C.

22. The method of claim 16, wherein the liquid salt is maintained at a temperature of about 600 C.

23. The method of claim 16, wherein the liquid metal is an alkali or alkaline earth metal or mixtures or alloys thereof.

24. The method of claim 16, wherein the liquid metal is Na or Mg.

25. The method of claim 16, wherein the liquid metal is removed from the vessel by suction with metal particulates being prevented from being removed with the liquid metal.

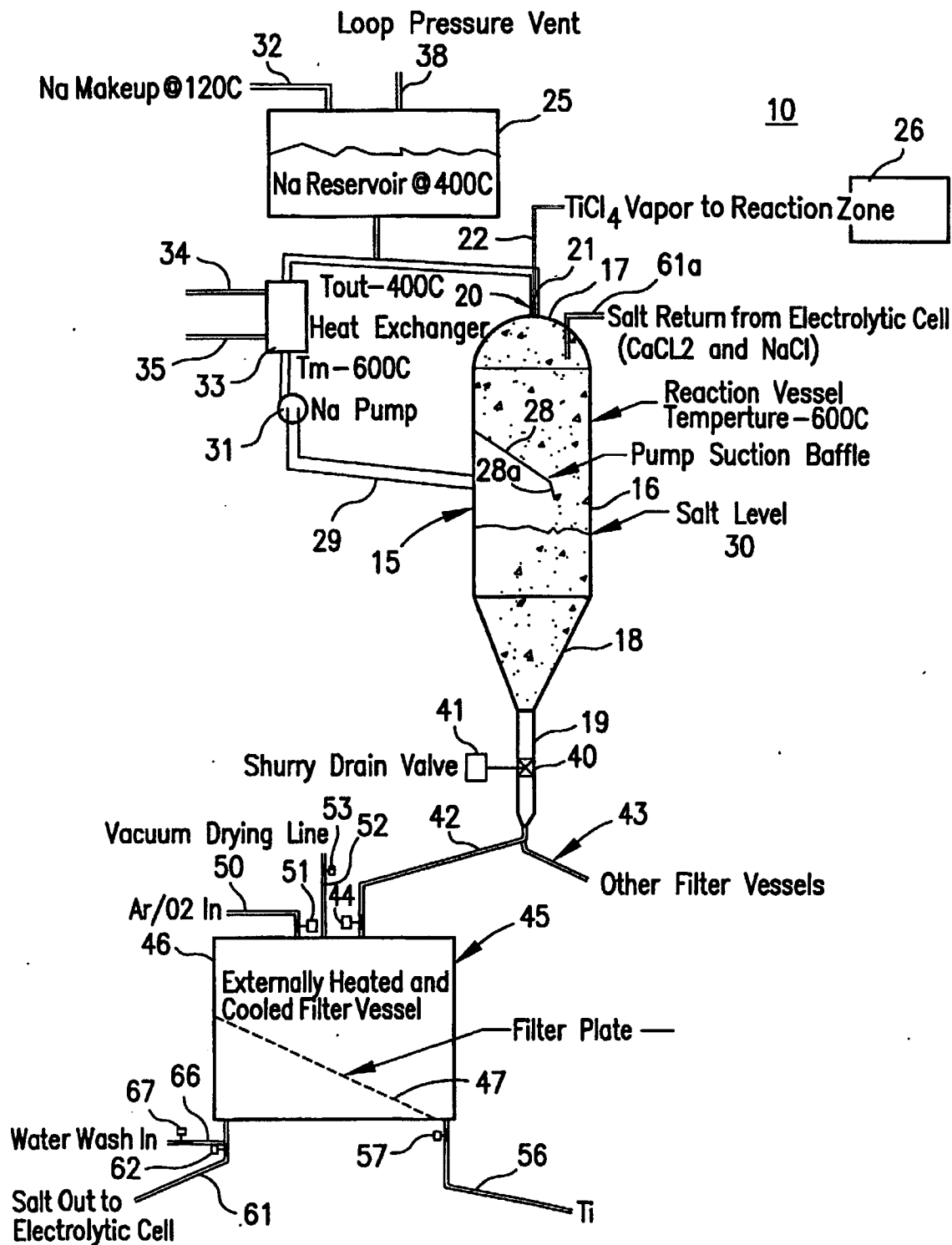


FIG. 1

SUBSTITUTE SHEET (RULE 26)

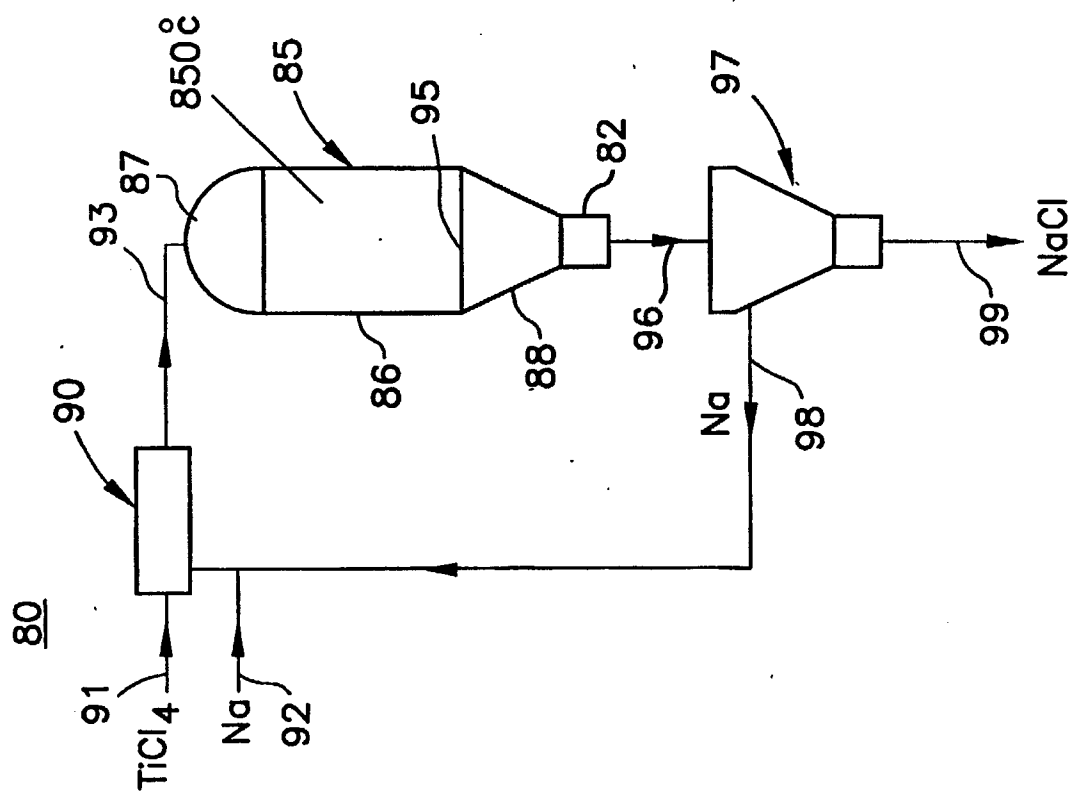


FIG. 2

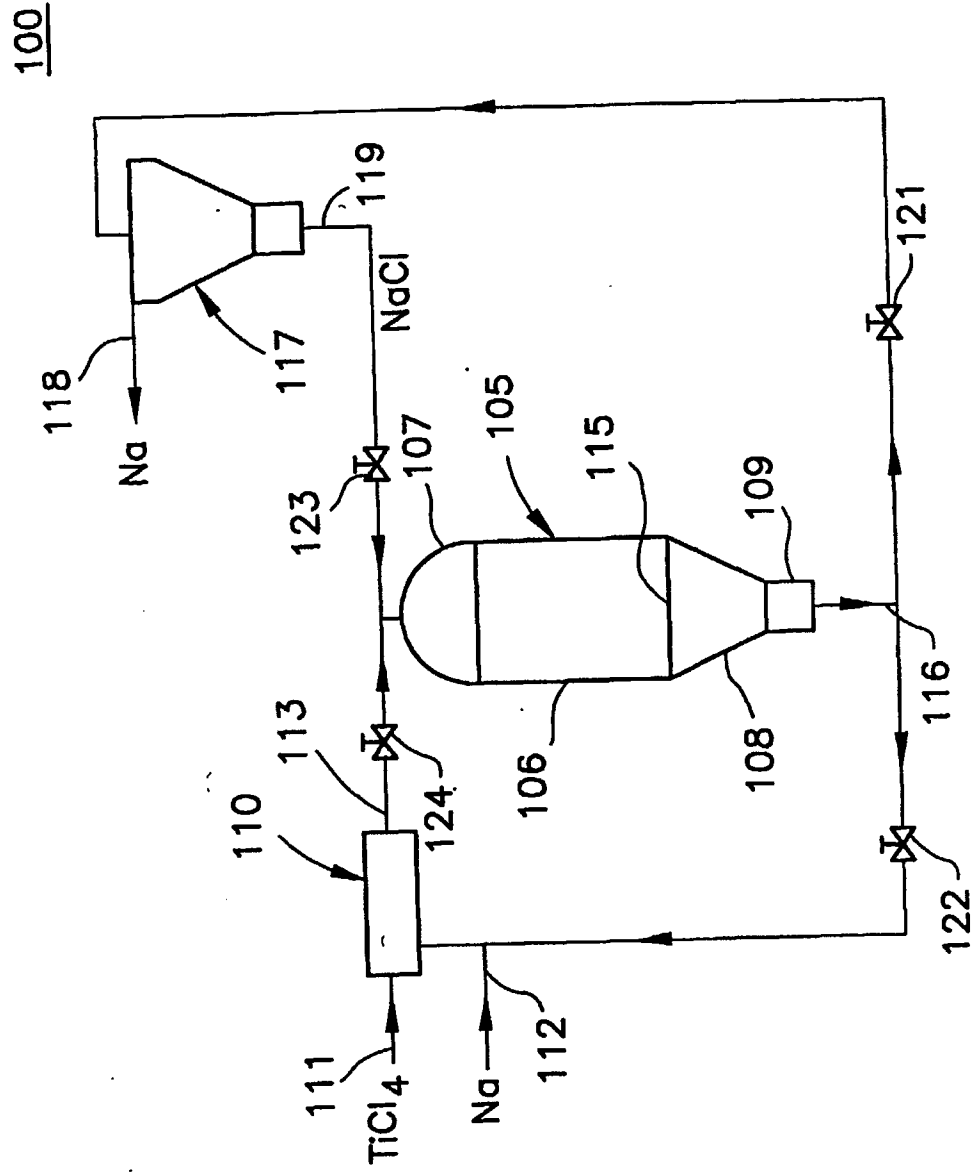


FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27785

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B34/12 C22B9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 915 382 A (RAYMOND PAUL L ET AL) 1 December 1959 (1959-12-01) column 2, line 57 - column 3, line 16 ---	1-25
A	US 2 823 991 A (JONAS KAMLET) 18 February 1958 (1958-02-18) claim 1; column 3, lines 33-57 ---	1-25
A	US 6 409 797 B2 (ANDERSON RICHARD PAUL ET AL) 25 June 2002 (2002-06-25) cited in the application column 4, lines 24-55 ---	1-25
A	US 4 379 718 A (GRANTHAM LEROY F ET AL) 12 April 1983 (1983-04-12) -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

20 January 2004

Date of mailing of the international search report

02/02/2004

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bjoerk, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 03/27785

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2915382	A	01-12-1959	NONE
US 2823991	A	18-02-1958	GB 770850 A 27-03-1957
US 6409797	B2	17-01-2002	US 5958106 A 28-09-1999
		US 5779761 A 14-07-1998	
		US 2002005090 A1 17-01-2002	
		US 2002148327 A1 17-10-2002	
		US 2002152844 A1 24-10-2002	
		US 2003145682 A1 07-08-2003	
		US 2003061907 A1 03-04-2003	
		AU 686444 B2 05-02-1998	
		AU 3320195 A 04-03-1996	
		BR 9508497 A 23-12-1997	
		CA 2196534 A1 15-02-1996	
		CN 1161064 A , B 01-10-1997	
		DE 69521432 D1 26-07-2001	
		DE 69521432 T2 29-05-2002	
		EP 0777753 A1 11-06-1997	
		ES 2161297 T3 01-12-2001	
		JP 10502418 T 03-03-1998	
		JP 3391461 B2 31-03-2003	
		KR 241134 B1 02-03-2000	
		NO 970444 A 26-03-1997	
		RU 2152449 C1 10-07-2000	
		WO 9604407 A1 15-02-1996	
US 4379718	A	12-04-1983	AU 543753 B2 02-05-1985
			AU 8346582 A 25-11-1982
			CA 1193447 A1 17-09-1985
			JP 1716294 C 27-11-1992
			JP 3080854 B 26-12-1991
			JP 57194220 A 29-11-1982

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
1 April 2004 (01.04.2004)

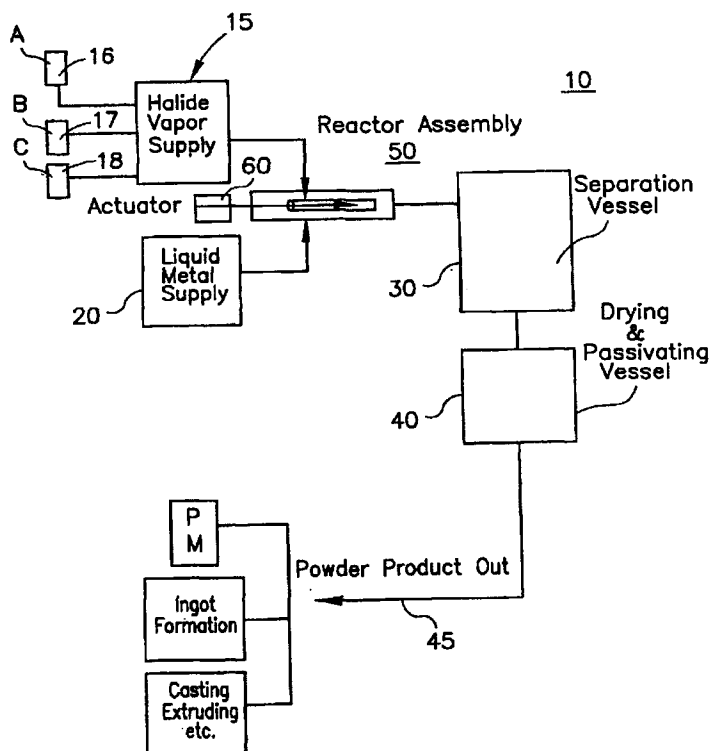
PCT

(10) International Publication Number
WO 2004/026511 A2

- (51) International Patent Classification⁷: **B22F 9/28**
- (21) International Application Number:
PCT/US2003/027648
- (22) International Filing Date:
3 September 2003 (03.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/408,924 7 September 2002 (07.09.2002) US
60/408,825 7 September 2002 (07.09.2002) US
- (71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **ANDERSON, Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). **ARMSTRONG, Donn** [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).
- (74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar, Suite 3000, 300 South Wacker Drive, Chicago, IL 60606 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR CONTROLLING THE SIZE OF POWDER PRODUCED BY THE ARMSTRONG PROCESS



(57) Abstract: A needle valve is disclosed for controlling the quantity of a halide vapor to be injected into a liquid metal. The needle valve may seat in a supersonic nozzle from which the halide vapor exits. Various products made with the apparatus of the invention are disclosed.



Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

- *without international search report and to be republished upon receipt of that report*

METHOD AND APPARATUS FOR CONTROLLING THE SIZE OF POWDER PRODUCED BY THE ARMSTRONG PROCESS

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application U.S. Provisional Application Serial No. 60/408,924 filed September 7, 2002 and U.S. Provisional Application Serial No. 60/408,825 filed September 7, 2002

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong process as described in 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. As illustrated in the above-referenced patents, a reductant metal and a halide of the metal to be produced are introduced into a reactor chamber. For instance, in the '106 patent, a sodium stream from a source of sodium is pumped by a pump 11 into a reaction chamber 14. Titanium tetrachloride from a source thereof is fed by a pump 21 to a boiler 22. From the boiler 22, titanium tetrachloride vapor is also pumped to the reaction chamber 14.

The present invention relates in general to the Armstrong Process as described above but also more specifically to the reactor used in converting a halide vapor into a powder, either of ceramic or metal or alloy. More particularly, the invention relates in part to a needle valve used to introduce halide vapor into the liquid metal, such as sodium, providing significant advantages to the Armstrong Process. In another aspect of the invention, a supersonic nozzle is used for the introduction of the halide vapor to improve the mixing of the vapor with the liquid, reducing the expansion of the gas into the liquid which occurs with a sonic nozzle, thereby modifying the reactions advantageously.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide an apparatus for injecting halide vapor into a liquid metal in which a needle valve is used to carefully meter the amount of vapor introduced into the liquid metal.

Still another object of the invention is to provide an apparatus for introducing a halide vapor into a liquid metal environment in which a supersonic nozzle is employed.

Another object of the invention is to provide an apparatus and system for injecting a halide vapor subsurface of a liquid metal, comprising inner and outer conduits forming an annulus there between, a needle valve interior of the inner conduit movable axially thereof between an open position in which the inner conduit is in fluid communication with the outer conduit and a closed position in which the inner conduit is sealed from the outer conduit, a supply of halide vapor in fluid communication with the inner conduit, a supply of liquid metal in fluid communication with the outer conduit, and an actuator assembly connected to the needle valve for moving the needle valve axially of the inner conduit between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in the annulus results in an exothermic reaction controlled at least in part by the axial position of the needle valve.

A still further object of the present invention is to provide an apparatus and system of the type set forth incorporating a supersonic nozzle.

Another object of the present invention is to provide a system for making a powder by the exothermic reduction of a halide vapor with an alkali metal or an alkaline earth metal or mixtures thereof, comprising a supply of liquid alkali or alkaline earth metal or mixtures thereof, a supply of a halide vapor, an apparatus for injecting the halide vapor subsurface of the liquid metal having inner and outer conduits forming an annulus therebetween, a needle valve interior of the inner conduit movable axially thereof between an open position in which the inner conduit is in fluid communication with the outer conduit and a closed position in which the inner conduit is sealed from the outer conduit, the supply of halide vapor being in fluid communication with the inner conduit, the supply of liquid metal in being fluid communication with the outer conduit, and an actuator assembly connected to the needle valve for moving the needle valve axially of the inner conduit between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in the annulus results in an exothermic reaction controlled at least in part by the axial position of the needle valve producing the powder and the halide salt of the liquid metal.

Still another object of the present invention is to provide a system of the type previously set forth using a supersonic nozzle without a needle valve to introduce the

halide vapor into the liquid metal.

A final object of the present invention is to provide powder made by the operation of the apparatus and systems disclosed, the powder being a ceramic, a metal or an alloy with or without conversion to a solid product from the powder.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of a system for practicing the present invention;

FIG. 2 is a schematic representation of a needle valve assembly useful in the present invention; and

FIG. 3 is a schematic representation of a supersonic nozzle useful in the practice of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to Figure 1 of the drawings, there is disclosed a system 10 for the practice of the present invention including a supply of halide vapor 15 which in turn is in fluid communication with a plurality of liquid halide or solid halide materials, shown for purposes of illustration only as supplies 16, 17 and 18 for halide liquids or solids A, B and C respectively. The system 10 further includes a supply of liquid metal 20 which may be any alkali or alkaline earth metal or various mixtures thereof, sodium and magnesium being preferred with sodium being mostly preferred.

Similarly, with respect to the halide vapor supply 15, chlorides are preferred.

There is further provided a separation vessel 30 in fluid communication with a reactor assembly 50, as will be described and the separation vessel 30 is also in fluid

communication with a drying and passivating vessel 40. A powder product outlet 45 is in fluid communication with the drying and passivating vessel 40, as will be described, is either the final product or the intermediate product of the system and process of the invention.

The present invention and system 10 includes the reactor assembly 50, as seen in Fig. 2, which has an outer cylinder 51 having an exit portion 52 which may be of reduced diameter or of the same diameter as the remainder of the outer cylinder or conduit 51, as preferred.

The reactor assembly 50 serves to receive the halide of the metal or ceramic to be produced and the liquid reducing metal and to introduce the halide in a controlled fashion subsurface of the reducing metal or into a stream of the reducing metal so that the temperature of the reaction is controlled, in part, by the excess of the reducing metal, all is taught in the above-referenced patents.

The reactor assembly 50 has one-half of a sealing ring 54 on the exit nozzle portion 52 to sealing engage another sealing ring (not shown) located in the vessel into which the exit portion 52 is positioned. The outer cylinder 51 also has a inlet nozzle portion 56 which terminates in an end 57. An actuator 60, either pneumatic or otherwise, as is known in the art, is in communication with the reactor assembly 50 and particularly the outer cylinder 51 as will be explained. The outer cylinder 51 also has a pressure tap 62 which may be for the introduction of an inert gas such as argon or to vent the assembly 50, if required, or to monitor the pressure within the outer cylinder 51. Also provided is a reducing metal inlet 64, in the illustration a sodium inlet. Both the pressure tap 62 and the reducing metal inlet 64 extend through the outer cylinder 51 and are sealed thereto.

A sealing ring is made up of mating halves 66 and 67 intermediate the actuator 60 and the exit nozzle portion 52 of the reactor assembly 50. A halide inlet tap 69 extends into the inlet nozzle portion 56 of the outer cylinder 51 and is sealed downstream of the inlet 69 by means of the sealing rings 66, 67 and is in fluid communication with a housing 79 which may be generally cylindrical in shape and extends from the sealing half ring 66 through the outer cylinder 51 and terminates at an end 81 having a valve seat therein.

A needle valve 75 includes an elongated cylindrical shaft portion 76 having a conical shape valve portion 77 and another end 78 in communication with the actuator 60. The halide inlet 69 introduces halide vapor into the chamber formed by the inlet nozzle portion 56 of the outer cylinder 51 and enters the housing 79 by virtue of the communication between the end of the housing 79 and the sealing rings 66, 67. The sodium entering through sodium inlet 64 is on the outside of the housing 79 and completely fills the outer cylinder 51 and flows axially of the outer cylinder. The longitudinal axial movement of the needle valve 75 by means of the actuator 60 causes the conical end portion 77 to seat within a valve seat in the end 81 of the housing 79, it being apparent to those of ordinary skill in the art that the diameter of the valve seat in the end 81 must be smaller than the diameter of the shaft portion 76 of the needle valve 75. Valve seats 81 between 1/8 and 3/8 inch have been used with the appropriate change in shaft portion 76.

As stated in the above referenced patents, it is important that no sodium be able to back up through the valve seat in the end 81 into the halide vapor supply. That necessity is accomplished by using at least sonic flow of the halide through reactor assembly 50 as taught in the referenced patent. As the actuator 60 is operated to move the shaft portion 76 axially of outer cylinder 51 to the right in Fig. 1 so that the conical portion 77 of the needle valve 75 begins to seat within the valve seat in the end 81, the amount or volume of halide vapor, such as titanium tetrachloride, introduced into the sodium or reducing metal inside the outer cylinder 51 is reduced or controlled permitting the operators of the system to vary the time and rate of delivery of the halide vapor. Another advantage of the needle valve 75 is that when the needle valve 75 is fully seated within the valve seat in the end 81, a vacuum may be drawn upstream of the nozzle or reactor assembly 50 before startup of the production of the metal by the exothermic reaction of the halide with the reducing metal.

Referring now to Figure 3, there is disclosed a supersonic nozzle 5 including an elongated housing 86 having a first larger diameter 87 and a throat 88. The terminal or distal diameter 89 is larger than the throat 88 and smaller than the internal diameter 87, all as well known in the art. Representative but not limiting dimensions are on Figure 3, the arrow 90 being indicative of the gas flow through the nozzle 85.

The use of a supersonic nozzle 85 distinguished to a sonic nozzle is an improvement to the process disclosed in the above captioned patents. The supersonic nozzle 85 alters the flow pattern of the halide gas flow 90 and permits the halide gas to flow at a higher velocity at the entry point to the reductant metal. Also, the use of a supersonic nozzle 85 reduces the expansion of the halide gas as it enters the reductant metal thereby altering the size and shape of the reaction zone.

More specifically, when using a sonic nozzle, the vapor exiting the nozzle is at an over pressure condition which causes it instantly to expand at the end of the nozzle as the gas enters the liquid reductant. The use of a supersonic nozzle 85 (Fig. 3), permits the gas to exit the nozzle without being in an over pressurized condition and without the subsequent expansion associated with a sonic nozzle. By virtue of the use of the supersonic nozzle 85, a modified reaction zone is obtained in which various size and morphology characteristics of the product powder are altered and may also reduce the oxygen content of the powder produced. Designs of supersonic nozzles 85 are well known, the Fig. 3 shows a nozzle 85 having slightly larger diameter exit point 89 than the smallest diameter of the nozzle throat 88. Specifically, the exit diameter 89 of the nozzle 85 is 0.239 inches plus or minus 0.002 inches, and the narrowest part of the throat 88 is 0.219 inches plus or minus 0.002 inches. The invention is applicable to reductions of various halides with a wide variety of reductant metals, all as set forth in the above three referenced patents.

Referring again to Fig. 1, it is seen that the powder product 45 discharged from the drying and passivating vessel 40 may be used as a product in and of itself or may be used in powder metallurgy to produce product or ingot or other means by which solid product is formed which also includes casting, extruding or other methods. Any solid product or object made from the powder 45 produced by the inventive system 10 is within the purview of the present invention.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. An apparatus for injecting a halide vapor subsurface of a liquid metal, comprising inner and outer conduits forming an annulus therebetween, a needle valve interior of said inner conduit movable axially thereof between an open position in which said inner conduit is in fluid communication with said outer conduit and a closed position in which said inner conduit is sealed from said outer conduit, a supply of halide vapor in fluid communication with said inner conduit, a supply of liquid metal in fluid communication with said outer conduit, and an actuator assembly connected to said needle valve for moving said needle valve axially of said inner conduit between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in said annulus results in an exothermic reaction controlled at least in part by the axial position of said needle valve.
2. The apparatus of claim 1, wherein said outer conduit terminates at a distance from said inner conduit at least about five times the diameter of said inner conduit.
3. The apparatus of claim 1, wherein said supply of halide vapor includes one or more of the halides of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.
4. The apparatus of claim 1, wherein said supply of halides includes one or more of the halides of Ti, Al, Ta, V, Zr, Nb, Mo, Ga, Re, or Si.
5. The apparatus of claim 1, wherein said supply of liquid metal contains one or more of Na or Mg.
6. The apparatus of claim 1, wherein said supply of halide vapor is exclusively a chloride.
7. The apparatus of claim 1, wherein said supply of halide vapor includes TiCl_4 .
8. The apparatus of claim 7, wherein said supply of liquid metal contains Na.
9. The apparatus of claim 8, wherein said supply of halide vapor also includes the chlorides of Al and V.
10. A powder made by the operation of the apparatus of claim 1 wherein, said liquid metal flows continuously through said outer conduit when halide vapor flows through said inner conduit, said liquid metal being present in excess of the

stoichiometric amount necessary to reduce the halide vapor.

11. The powder of claim 10, wherein the powder is a metal or an alloy.
12. The powder of claim 10, wherein the powder is a ceramic.
13. A solid product made from the powder of claim 10.
14. An apparatus for injecting a halide vapor subsurface of a liquid metal, comprising inner and outer conduits forming an annulus therebetween, said inner conduit having an end forming a supersonic nozzle terminating within said outer conduit, a valve in communication with said inner conduit movable between an open position in which said inner conduit is in fluid communication with said outer conduit and a closed position in which said inner conduit is sealed from said outer conduit, a supply of halide vapor in fluid communication with said inner conduit, a supply of liquid metal in fluid communication with said outer conduit, and an actuator assembly connected to said valve for moving said valve between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in said annulus through said supersonic nozzle results in an exothermic reaction controlled at least in part by the position of said needle valve.
15. The apparatus of claim 14, wherein said supply of halide vapor includes one or more of the halides of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.
16. The apparatus of claim 15, wherein said supply of liquid metal contains one or more of Na or Mg.
17. The apparatus of claim 16, wherein said supply of halide vapor includes TiCl_4 .
18. The apparatus of claim 17, wherein said supply of liquid metal is Na.
19. The apparatus of claim 18 wherein said supply of halide vapor also includes the chlorides of Al and V.
20. A powder made by the operation of the apparatus of claim 14, wherein, said liquid metal flows continuously through said outer conduit when halide vapor flows through said inner conduit, said liquid metal being present in excess of the stoichiometric amount necessary to reduce the halide vapor.
21. The powder of claim 20, wherein the powder is a metal or an alloy or a ceramic.
22. A solid product made from the powder of claim 20.

23. An apparatus for injecting a halide vapor subsurface of a liquid metal, comprising inner and outer conduits forming an annulus therebetween, said inner conduit having an end forming a supersonic nozzle terminating within said outer conduit, a needle valve in communication with said inner conduit movable axially thereof between an open position in which said inner conduit is in fluid communication with said outer conduit and a closed position in which said inner conduit is sealed from said outer conduit, a supply of halide vapor in fluid communication with said inner conduit, a supply of liquid metal in fluid communication with said outer conduit, and an actuator assembly connected to said needle valve for moving said needle valve axially between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in said annulus through said supersonic nozzle results in an exothermic reaction controlled at least in part by the axial position of said needle valve.

24. The apparatus of claim 23, wherein said supply of halide vapor includes one or more of the chloride of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.

25. The apparatus of claim 24, wherein said supply of liquid metal contains one or more of Na or Mg.

26. The apparatus of claim 25, wherein said supply of halide vapor includes TiCl_4 and said liquid metal is Na.

27. The apparatus of claim 24, wherein said supply of halide vapor also includes the chlorides of Al and V.

28. A powder made by the operation of the apparatus of claim 26, wherein said liquid metal flows continuously through said outer conduit when halide vapor flows through said inner conduit, said liquid metal being present in excess of the stoichiometric amount necessary to reduce the halide vapor.

29. The apparatus of claim 28, wherein said powder is a metal or an alloy or a ceramic.

30. A solid product made from the powder of claim 29.

31. A system for making a powder by the exothermic reduction of a halide vapor with an alkali metal or an alkaline earth metal or mixtures thereof, comprising a supply of liquid alkali or alkaline earth metal or mixtures thereof, a supply of a halide vapor, an apparatus for injecting the halide vapor subsurface of the liquid metal having

inner and outer conduits forming an annulus therebetween, a needle valve interior of said inner conduit movable axially thereof between an open position in which said inner conduit is in fluid communication with said outer conduit and a closed position in which said inner conduit is sealed from said outer conduit, the supply of halide vapor being in fluid communication with said inner conduit, the supply of liquid metal in being fluid communication with said outer conduit, and an actuator assembly connected to said needle valve for moving said needle valve axially of said inner conduit between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in said annulus results in an exothermic reaction controlled at least in part by the axial position of said needle valve producing the powder and the halide salt of the liquid metal.

32. The system of claim 31, wherein said liquid metal is Na or Mg.

33. The system of claim 32, wherein said halide is a chloride.

34. The system of claim 33, wherein said supply of halide vapor includes one or more of the halides of Ti, Al, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, or Si.

35. The system of claim 34, wherein chloride is one or more of Ti, Al and V.

36. The method of claim 33, wherein, said liquid metal flows continuously through said outer conduit when halide vapor flows through said inner conduit, said liquid metal being present in excess of the stoichiometric amount necessary to reduce the halide vapor.

37. The method of claim 36, wherein the powder is a metal or an alloy or a ceramic.

38. A solid product made from the powder of claim 37.

39. A system for making a powder by the exothermic reduction of a halide vapor with an alkali metal or an alkaline earth metal or mixtures thereof, comprising a supply of liquid alkali or alkaline earth metal or mixtures thereof, a supply of a halide vapor, an apparatus for injecting the halide vapor subsurface of the liquid metal having inner and outer conduits forming an annulus therebetween, said inner conduit having an end forming a supersonic nozzle terminating within said outer conduit, a valve interior of said inner conduit movable between an open position in which said inner conduit is in fluid communication with said outer conduit and a closed position in which said inner conduit is sealed from said outer conduit, the supply of halide vapor being in fluid

communication with said inner conduit, the supply of liquid metal in being fluid communication with said outer conduit, and an actuator assembly connected to said valve for moving said needle valve between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in said annulus results in an exothermic reaction controlled at least in part by said needle valve producing the powder and the halide salt of the liquid metal.

40. A system for making a powder by the exothermic reduction of a halide vapor with an alkali metal or an alkaline earth metal or mixtures thereof, comprising a supply of liquid alkali or alkaline earth metal or mixtures thereof, a supply of a halide vapor, an apparatus for injecting the halide vapor subsurface of the liquid metal having inner and outer conduits forming an annulus therebetween, said inner conduit having an end forming a supersonic nozzle terminating within said outer conduit, a needle valve interior of said inner conduit movable axially thereof between an open position in which said inner conduit is in fluid communication with said outer conduit and a closed position in which said inner conduit is sealed from said outer conduit, the supply of halide vapor being in fluid communication with said inner conduit, the supply of liquid metal in being fluid communication with said outer conduit, and an actuator assembly connected to said needle valve for moving said needle valve axially of said inner conduit between the open and sealed positions thereof, whereby introduction of halide vapor into liquid alkali or alkaline earth metal or mixtures thereof present in said annulus through said supersonic nozzle results in an exothermic reaction controlled at least in part by the axial position of said needle valve producing the powder and the halide salt of the liquid metal.

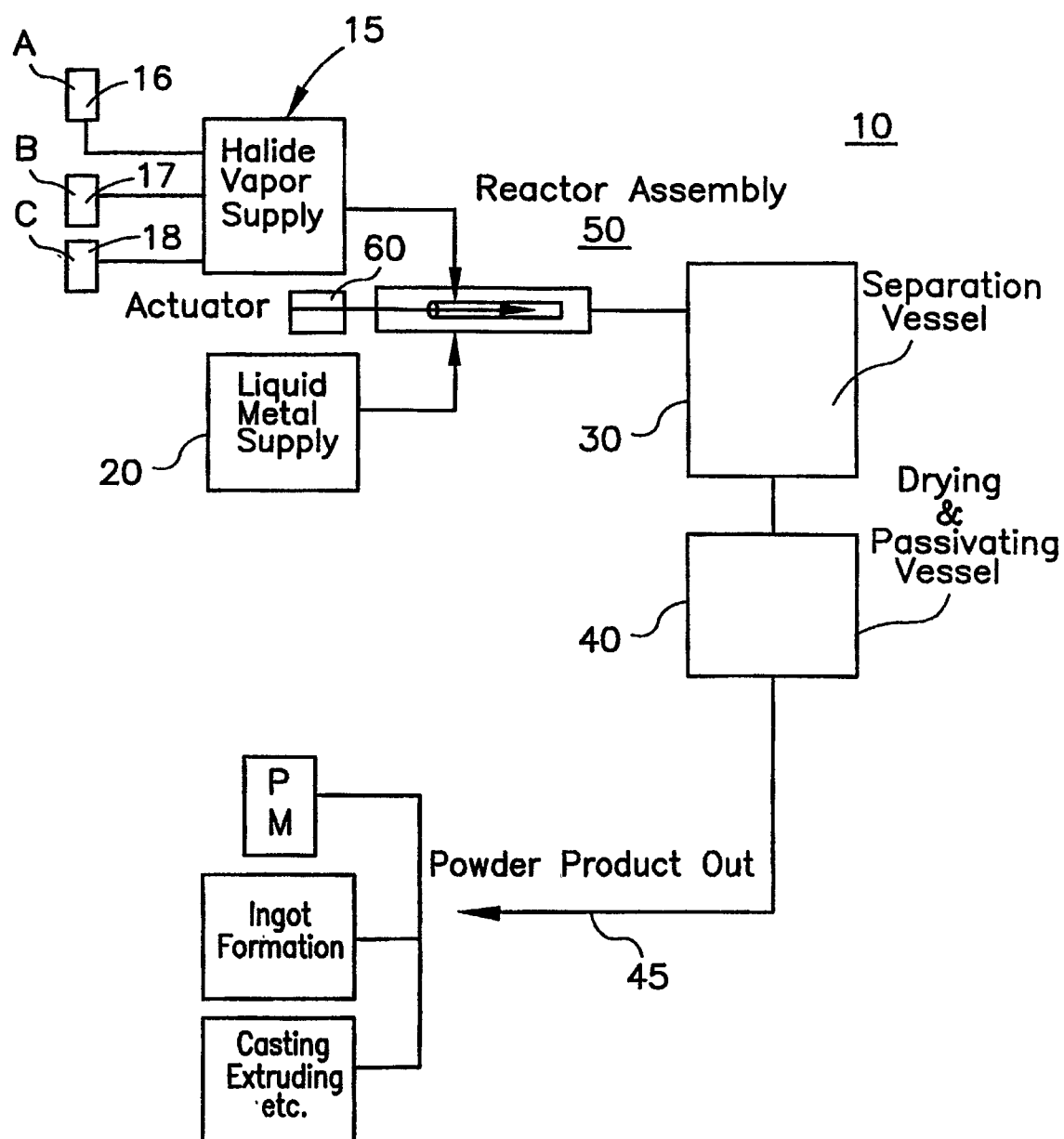


FIG. 1

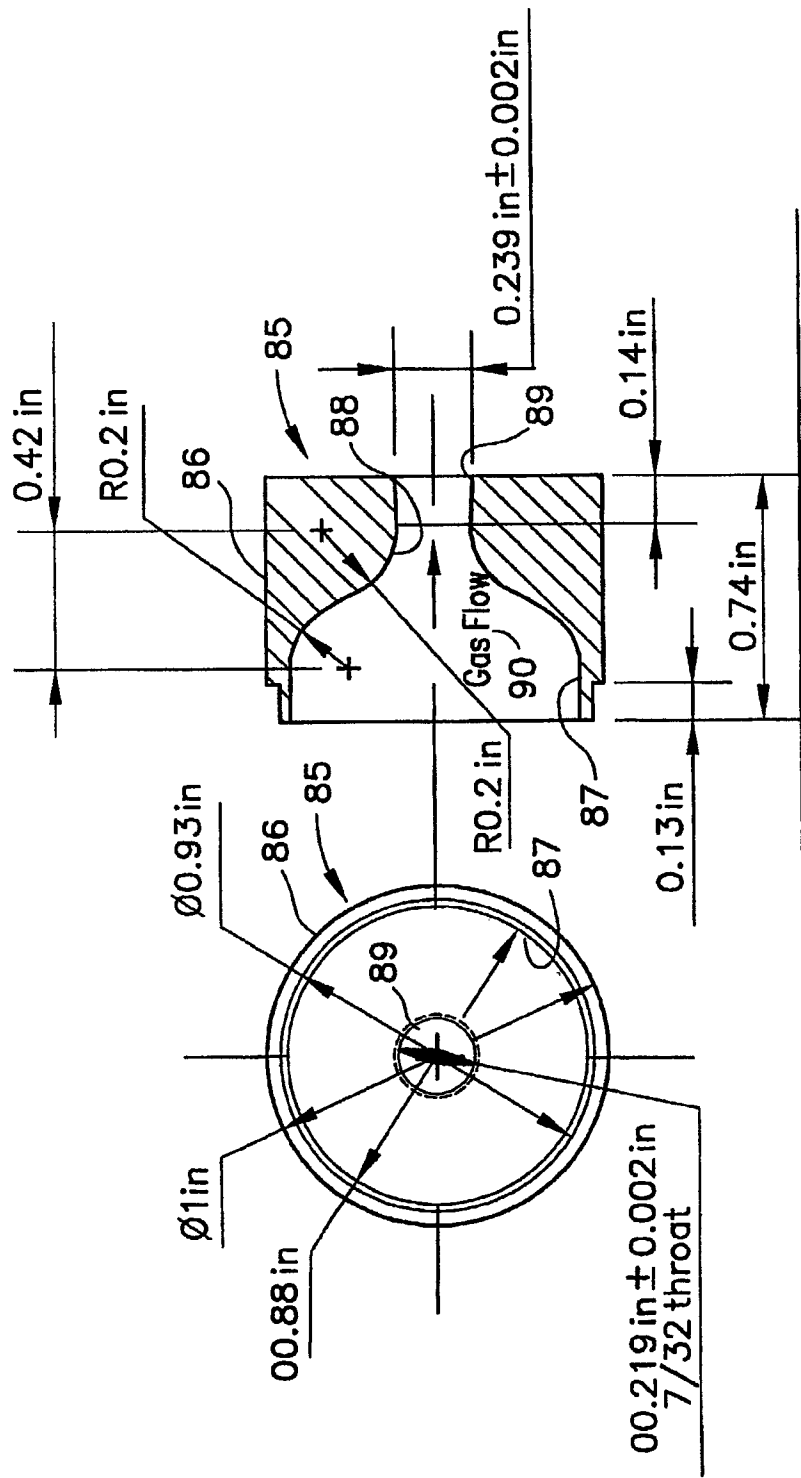


FIG. 3

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
8 April 2004 (08.04.2004)

PCT

(10) International Publication Number
WO 2004/028655 A2

(51) International Patent Classification⁷: **B01D**

(21) International Application Number:
PCT/US2003/027653

(22) International Filing Date:
3 September 2003 (03.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/408,920 7 September 2002 (07.09.2002) US
60/408,824 7 September 2002 (07.09.2002) US
60/408,952 7 September 2002 (07.09.2002) US

(71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ANDERSON, Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills,

IL 60514 (US). **ARMSTRONG, Donn** [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).

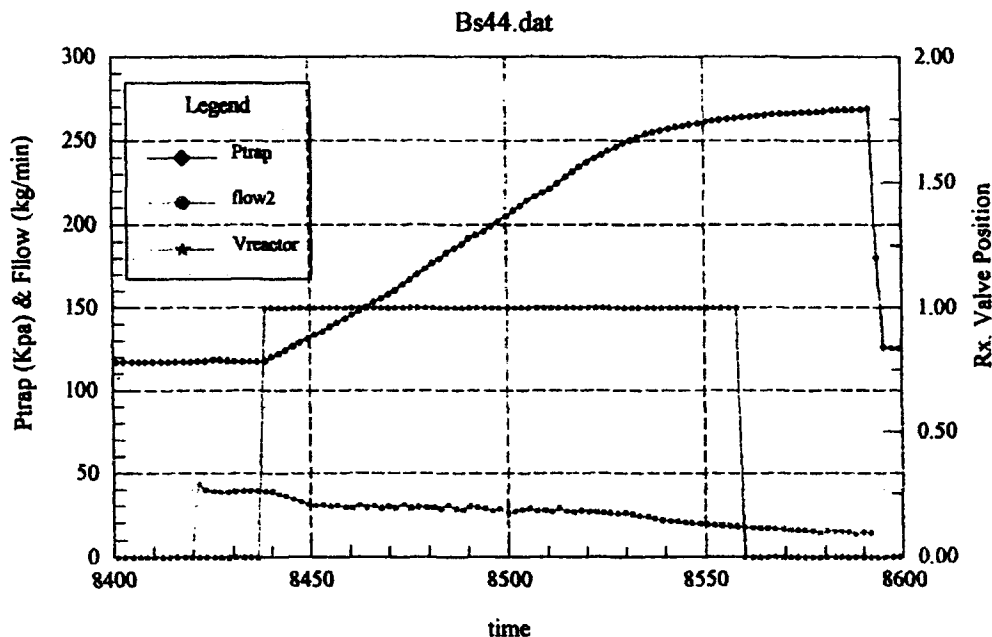
(74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar, 300 South Wacker Drive, Suite 3000, Chicago, IL 60606 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: FILTER CAKE TREATMENT APPARATUS AND METHOD



(57) Abstract: A method of separating metal particulates from a slurry of liquid metal and metal particulates and salt particulates by filtering the slurry to form a cake of metal and salt particulates with some liquid metal. The cake is broken and liquid metal is removed by vacuum distillation or with a hot inert sweep gas at either position or negative pressure from the broken cake, and thereafter separating the metal and salt particulates. Thereafter, the metal particulates are sized before water washing to prevent unacceptable explosions upon contact with water.



Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

FILTER CAKE TREATMENT APPARATUS AND METHOD**RELATED APPLICATIONS**

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application serial No. 60/408,920, filed September 7, 2002, U.S. Provisional Application Serial No. 60/408,824, filed September 7, 2002 and U.S. Provisional Application Serial No. 60/408,952, filed September 7, 2002

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong process as described in U.S. patents 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. In the production of a metal or alloy or other elemental material as described in the above-referenced patents, a slurry is produced which if filtered provides a filter cake in the form of a gel. The slurry has a solids fraction which depends in large part on the amount of excess reductant metal used to control the steady-state temperatures at which the reaction runs. As liquid metal drains through the filter to build the filter cake, a gel is formed from which particles do not settle, unless the gel is broken, such as by mechanical disturbance or other means. The gel when formed includes the metal particles formed during the reduction, the salt particles formed during the reduction and interstitial liquid metal. The liquid metal in the gel has to be removed by way of distillation with or without a vacuum or by contact with a hot sweep gas, preferably inert to the constituents of the gel with or without a vacuum or any combination thereof.

SUMMARY OF THE INVENTION

In the specific example of the patents, liquid sodium is used as a reducing metal, and titanium tetrachloride as the source of the halide vapor to produce titanium powder. However, this invention pertains to any product produced by the Armstrong Process. The gel, therefore in this specific example, is liquid sodium, salt (NaCl) particles and titanium powder or particulates.

In one instance of treatment of the filter cake and gel, vacuum distillation of the filter cake typically results in an initial temperature rise in the cake which thereafter holds constant and a constant pressure for a long period of time, such as about 40,000 seconds (about 11 hours) to about 50,000 seconds (about 14 hours), at current typical temperatures and pressures of about 550°C and about 50 millitorr. Thereafter, there is a long tail of decreasing temperature and pressure, also about 40,000 seconds (about 11 hours) to about 50,000 seconds (about 14 hours) to distill sufficient sodium from the gel until the gel is ready for additional processing. Accordingly, the first portion of the distill may take between about 11 and 14 hours and the same for the tail portion of the distill. It is understood by those of ordinary skill in the art that distillation of the tail may not be able completely to remove all the liquid metal trapped in the interstices of the metal powder and salt, so that some very small amount of liquid sodium may remain even after the distill shows that no more liquid metal is being distilled.

A series of graphs attached hereto show the relationship between pressure and time as well as a partial cross-sectional view of the filter trap showing the cake and the mechanism for distilling sodium.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

Fig. 1 is a graph of pressure rise versus time for a flat plate filter nutsche runs;
Fig. 2 shows data for various temperatures as a function of time and pressure;
Fig. 3 shows a schematic of the filter trap for the above example; and
Fig. 4 shows a schematic of another embodiment of the filter trap of Fig. 3.

DESCRIPTION OF THE PREFERRED EMBODIMENT

P-trap is the pressure above the filter (assume downstream pressure remains constant) as the run progressed. Flow 2 is the Na flow rate and the V reactor shows when the product was made. At t=8420, sodium flow was initiated to the trap. Trap pressure remained relatively constant as the Na flowed through the clean filter (125 micron) until the reactor valve was opened and started to build cake. The cake DP grew in a linear fashion until t=8520 when the reaction rate began to slow because of nozzle plugging due to subsonic operation of the nozzle. The cake thickness after distillation was measured to be on average 5 to 6 inches. The bottom of the cake appeared less dense than the top of the cake and measurements of the cake density showed a density in the top of the cake of 1.1 g/cc and in the bottom of the cake .73 g/cc. It is believed that the bottom was less dense because it was formed at a lower pressure. For example, the DP is determined by the flow rate; for this run the flow rate was 30 kg/min. Also, after product production was terminated and Na flow continued, the cake appeared to compact further (see pressure increase while flow decreased after t=8550). Prior to Na flow shutdown, DP was up to 22 psig versus 18 psig when significant product production ended, see Figs. 1 and 2.

Heat was applied to the cake area and vapor was removed to a primary condenser out the top side of the trap and to a secondary condenser by distilling through the wedge wire filter. During the distillation, a total of 5.9 kg of Na was removed from the cake which weighed 3.4 kg after the distill. 3.8Kg of the 5.9 kg was found to have condensed in the secondary condenser, see Fig. 3.

In another nutsche run, the trap was designed to allow distillation through the filter into the bottom of the trap to utilize the full trap diameter for vapor movement. The trap also had the standard 1" line to a primary condenser, see Fig. 4. Heat was

concentrated on the cake area while the bottom of the trap was maintained cool to support condensation of the Na. After distillation, 1.6 kg of Na went to the primary condenser and 1.3 kg. of Na distilled into the bottom of the trap leaving a 3.1 kg. cake of titanium and NaCl.

However, it has been found that breaking the filter cake drastically reduces the distillation times and rates for the distillation of the liquid metal, such as sodium. Using a breaker bar or some other mechanical means such as moving fingers or a mixer has significantly reduced the first portion of the vacuum distill from 40,000 - 50,000 seconds (11-14 hours) to 20,000 to 30,000 (between about 6 and 8 hours). The second portion of the distill, that is the decreasing temperature and pressure portion referred to as the tail was not affected by breaking the filter cake.

It has also been discovered that using a sweep of inert gas such as argon heated, preferably in the range of from about 500°C to about 800°C. during the second distill or tail portion reduced the amount of time necessary to distill the reductant metal (sodium) from about 40,000 - 50,000 seconds to about 10,000 seconds (about 3 hours.). This is a significant improvement over the prior method. By using either one of the methods or a combination of breaking the filter cake combined with an inert gas sweep, the distillation times can be decreased from about (22 or 28) hours to about (9 to 11) hours. This is of significant importance in the design of plants by simplifying designs, reducing collection tanks, valves, piping and other associated equipment. After vacuum distillation is apparently complete, any remaining trapped reductant metal (sodium) becomes impractical to remove. While it seems obvious to introduce the filter cake into water to wash the residual salt (NaCl) from the titanium powder, the problem exists of trapped reductant metal (sodium) in the filter cake which when combined with water could produce a significant explosion. It is a fact that the mixture of sodium liquid and water will provide an explosion having energy greater than the equivalent amount of TNT.

It has been found in the production of Ti by the subsurface reduction of TiCl_4 by Na that crumbling the filter cake into small quantities, such as less than about five centimeters in diameter and preferably in the range of from about two to about five centimeters in diameter, during or subsequent to the distillation of sodium apparently makes particles or clumps small enough that any trapped Na is manageable without significant damage to equipment or harm to personnel, if proper care is taken in equipment design and with appropriate safety precautions. After distillation, the filter cake is friable and easily crumbled. To the extent that large quantities of crumbled filter cake can be water washed without fear of explosion significantly reduces the distillation times required in the production of the various elemental material and alloys described in the above-referenced patents, particularly where sodium or other alkaline metal is used as a reductant.

Alternatively, it has been found that the entire distillation can be accomplished at positive pressure, such as, but not limited to, psig with a heated or hot inert gas, such as but not limited to Ar at about 500°C to about 800°C followed by cooling to condense the vaporized liquid metal, such as but not limited to Na. Thereafter, the cooled liquid metal will be returned for additional use.

Summarizing this invention relates to mechanism and methods for decreasing the distillation time of a filter cake produced by the process described in the above-referenced patents. The filter cake can be broken such as by vibration or moving mechanism in the filter cake area or by stationery mechanical bars or members in the filter cake area or other suitable mechanism. An inert sweep gas with or without vacuum can be used alone or in combination with the above described methods breaking the filter cake during the distillation in order significantly to reduce the distillation time of the liquid metal in the filter cake.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WE CLAIM:

1. A method of separating metal particulates from a slurry of liquid metal and metal particulates and salt particulates, comprising filtering the slurry to form a cake of metal and salt particulates with some liquid metal, breaking the cake and removing liquid metal from the broken cake, and thereafter separating the metal and salt particulates.

2. The method of claim 1, wherein the liquid metal is removed from the broken cake by vacuum distillation.

3. The method of claim 1, wherein the liquid metal is removed from the broken cake with a hot sweep gas.

4. The method of claim 3, wherein the hot sweep gas is an inert gas.

5. The method of claim 4, wherein the inert gas is argon.

6. The method of claim 4, wherein the hot sweep gas is at positive pressure.

7. The method of claim 5, wherein the hot argon sweep gas is at positive pressure.

8. The method of claim 1, wherein the liquid metal is present in the filter cake up to about ten times the weight of the metal particulates.

9. The method of claim 1, wherein the liquid metal is an alkali metal or an alkaline earth metal or mixtures thereof.

10. The method of claim 1, wherein the liquid metal is Na or Mg.

11. The method of claim 1, wherein the metal particulates are Ti.

12. The method of claim 1, wherein the metal particulates are a Ti alloy.

13. The method of claim 1, wherein the salt particulates are a halide.

14. The method of claim 1, wherein the salt particulates are a chloride.

15. The method of claim 1, wherein the metal particulates are Ti or a Ti alloy and the salt is Na or Mg chloride.

16. The method of claim 15, wherein the liquid metal is Na and the salt particulates are NaCl.

17. The method of claim 1, wherein the cake is broken into pieces having diameters up to about five centimeters.

18. The method of claim 1, wherein the cake is broken into pieces having diameters up to about two centimeters.

19. A method of separating metal particulates from a slurry of liquid metal and metal particulates and salt particulates, comprising filtering the slurry to form a cake of metal and salt particulates with some liquid metal, breaking the cake and removing liquid metal from the broken cake, separating the metal and salt particulates, and sizing the metal particulates before water washing to prevent unacceptable explosions upon contact with water.

20. The method of claim 19, wherein the liquid metal is removed from the broken cake by vacuum distillation or by a hot sweep gas.

21. The method of claim 20, wherein the hot sweep gas is argon.

22. The method of claim 20, wherein the hot sweep gas is at positive pressure.

23. The method of claim 21, wherein the hot argon sweep gas is at positive pressure.

24. The method of claim 20, wherein the liquid metal is Na or Mg and is present in the filter cake up to about ten times the weight of metal particulates.

25. The method of claim 24, wherein the metal particulates are Ti or a Ti alloy.

26. The method of claim 25, wherein the cake is broken into pieces having diameters up to about five centimeters.

27. The method of claim 26, wherein the cake is broken into pieces having diameters up to about two centimeters.

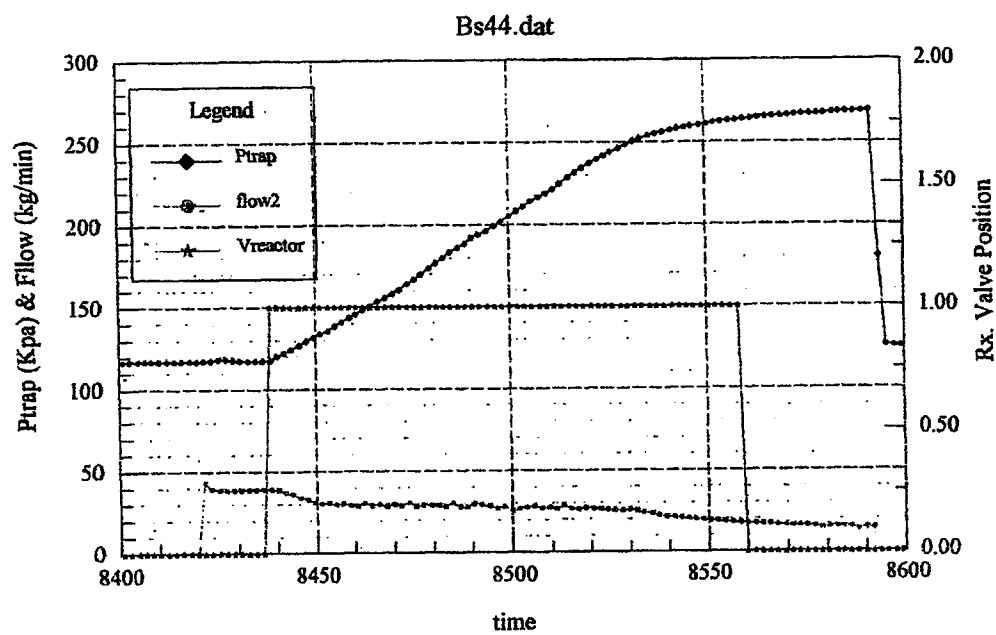
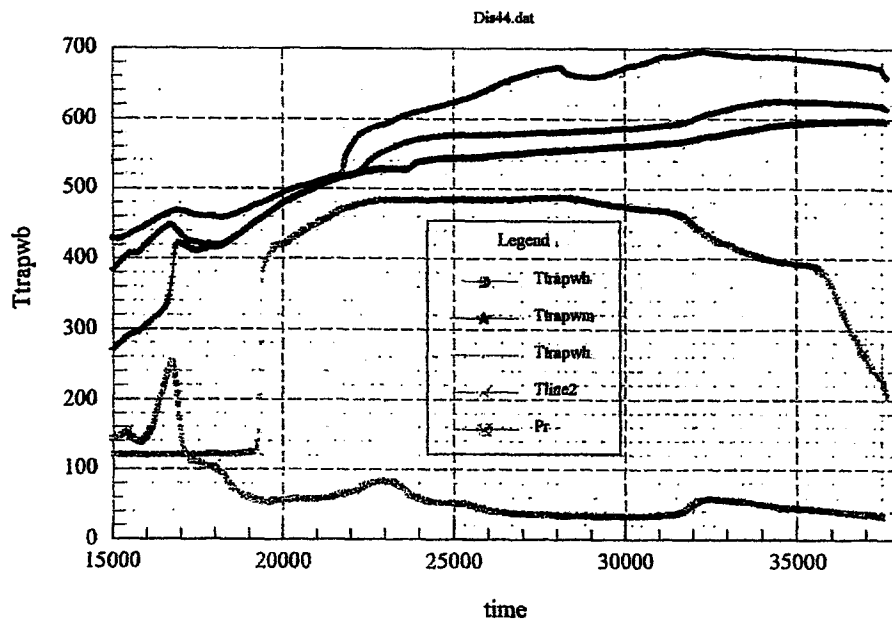


Fig.1

The distill data for this run (BS44) is shown in the following graph.



TTrapwb, wm and wh are vessel wall temperatures at the bottom, middle, and top of the trap, Tline2 is a primary condenser line temperature (c) and Pr is the vacuum (mtorr).

Fig. 2

The distillation setup for this trap was as follows:

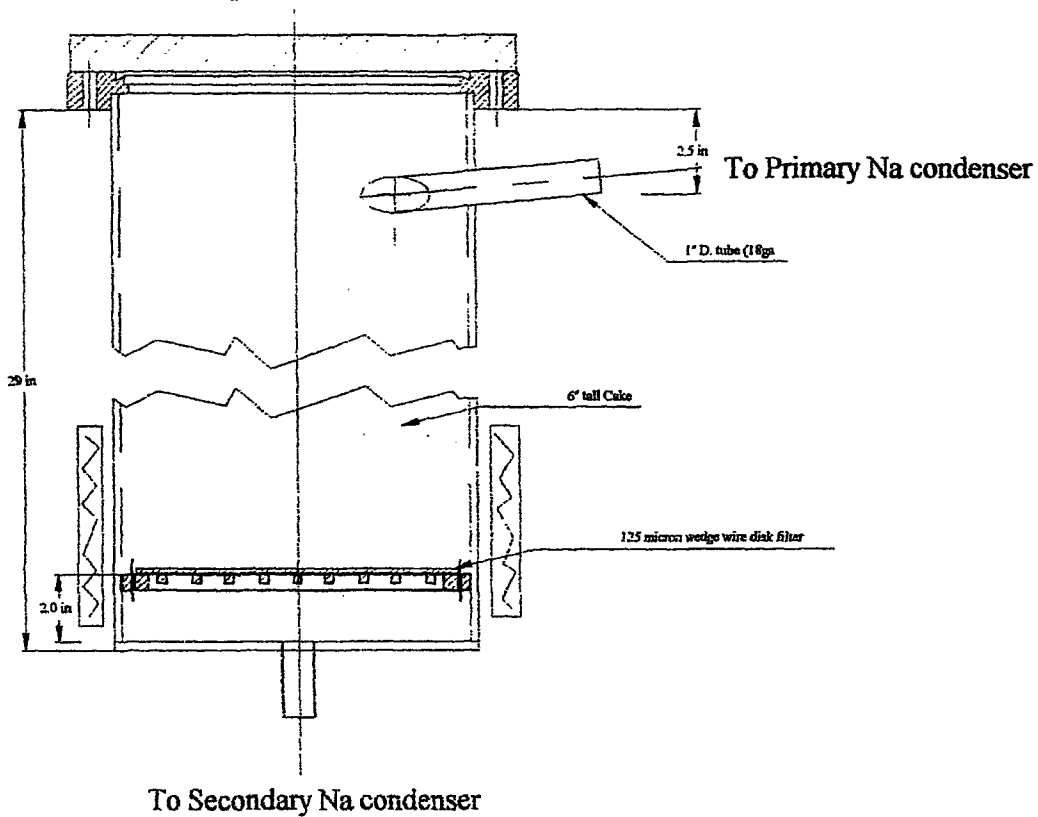
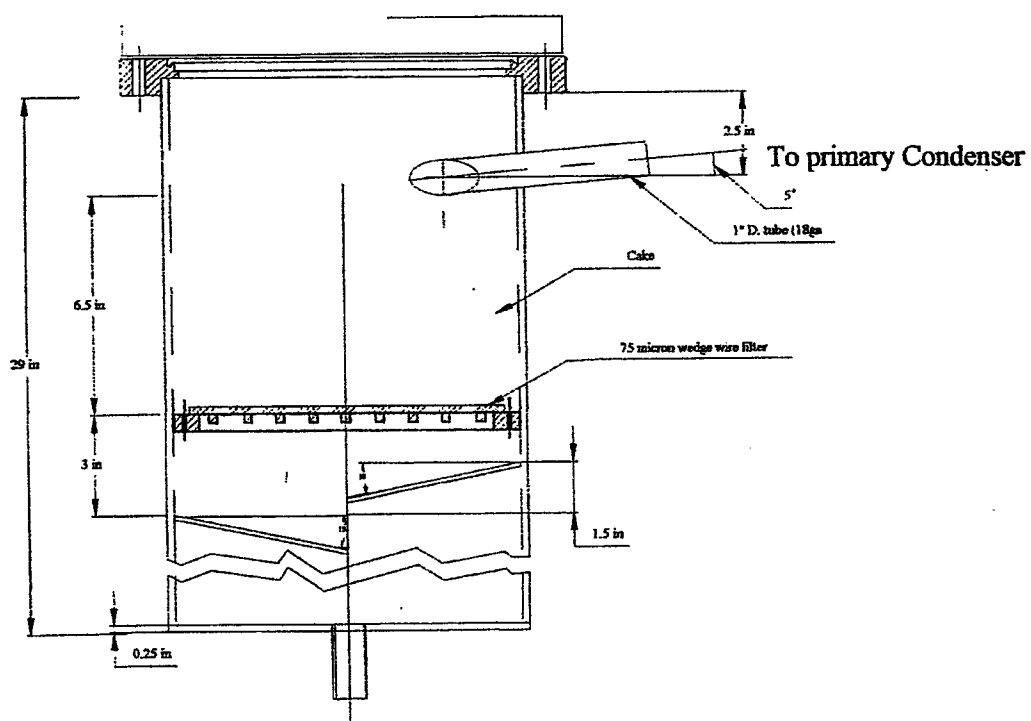


Fig.3



After the distillation, 1.6kg of na went to the primary condenser and 1.3kg of Na distilled into the bottom of the trap leaving a 3.1kg cake of Ti and NaCl.

Fig. 4

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number
WO 2004/033736 A1

(51) International Patent Classification⁷: C22B 34/12,
B22F 9/28, C22C 1/04

(21) International Application Number:
PCT/US2003/027651

(22) International Filing Date:
3 September 2003 (03.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/416,630 7 October 2002 (07.10.2002) US

(71) Applicant (for all designated States except US): INTER-
NATIONAL TITANIUM POWDER, LLC. [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): ANDERSON,
Richard [US/US]; 5836 Sunrise Avenue, Clarendon Hills,
IL 60514 (US). ARMSTRONG, Donn [US/US]; 6005
Ridge Court, Lisle, IL 60532 (US). JACOBSEN, Lance
[US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).

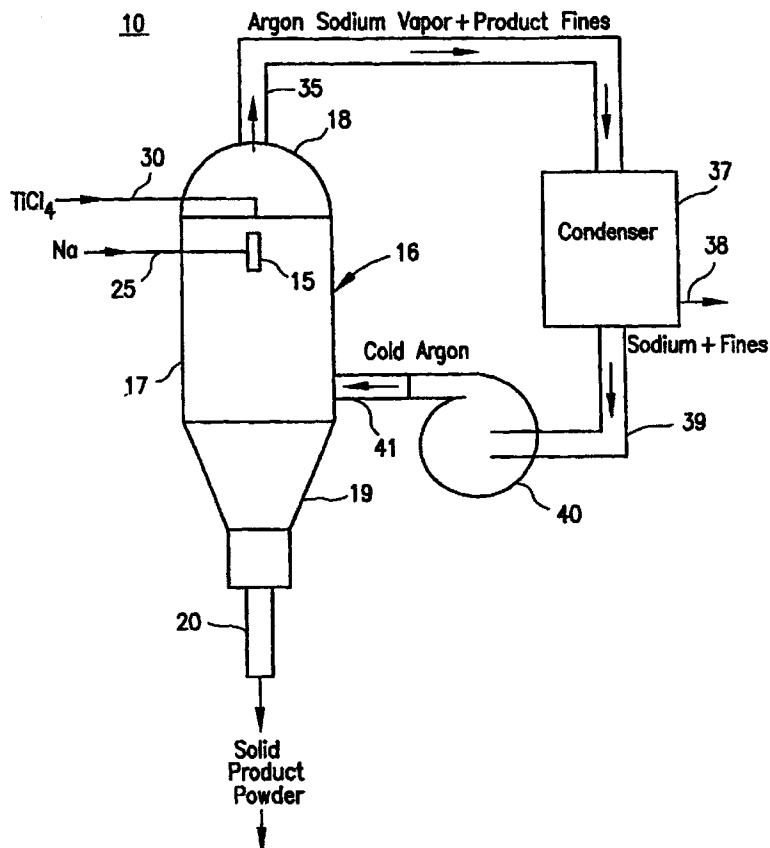
(74) Agent: LEVY, Harry, M.; Emrich and Dithmar, 300
South Wacker Drive, Suite 3000, Chicago, IL 60606 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),

[Continued on next page]

(54) Title: SYSTEM AND METHOD OF PRODUCING METALS AND ALLOYS



(57) Abstract: A system and method of producing an elemental material or an alloy from a halide of the elemental material or halide mixtures. The vapor halide of an elemental material or halide mixtures are introduced into a liquid phase of a reducing metal of an alkali metal or alkaline earth metal or mixtures thereof present in excess of the amount needed to reduce the halide vapor to the elemental material or alloy resulting in an exothermic reaction between the vapor halide and the liquid reducing metal. Particulates of the elemental material or alloy and particulates of the halide salt of the reducing metal are produced along with sufficient heat to vaporize substantially all the excess reducing metal. Thereafter, the vapor of the reducing metal is separated from the particulates of the elemental material or alloy and the particulates of the halide salt of the reducing metal before the particulate reaction products are separated from each other.



Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *with international search report*

SYSTEM AND METHOD OF PRODUCING METALS AND ALLOYS

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on U.S. Provisional Application Serial No. 60/416,630 October 7, 2002 and U.S. Provisional Application Serial No. 60/328,022 filed October 9, 2001.

BACKGROUND OF THE INVENTION

This invention relates to the production and separation of elemental material from the halides thereof and has particular applicability to those metals and non metals for which a reduction of the halide to the element is exothermic. Particular interest exists for titanium, and the present invention will be described with particular reference to titanium, but is applicable to other metals and non metals such as aluminum, arsenic, antimony, beryllium, boron, tantalum, gallium, vanadium, niobium, molybdenum, iridium, rhenium, silicon osmium, uranium, and zirconium, all of which produce significant heat upon reduction from the halide to the metal. For the purposes of this application, elemental materials include those metals and non metals listed above or in Table 1 and the alloys thereof.

This invention is an improvement in the separation methods disclosed in U.S. patent no. 5,779,761, U.S. patent no. 5,958,106 and U.S. patent no. 6,409,797, the disclosures of which are incorporated herein by reference. The above-mentioned '761, '106 and '797 patents disclose a revolutionary method for making titanium which is satisfactory for its intended purposes and in fact continuously produces high grade titanium and titanium alloys. However, the method described in the '761 patent, the '106 and the '797 patent produces a product which includes excess liquid reducing metal. The present invention resides the discovery that by maintaining the excess reducing metal in vapor phase by controlling the temperature of reaction and the amount of excess reducing metal, the separation of the produced material is made easier and less expensive.

More particularly, it has been found that by controlling the amount of excess metal, the temperature of the reaction products of the exothermic reaction can be maintained between the boiling point of the reducing metal and the boiling point of the salt produced which causes excess reducing metal to remain in the vapor

phase after the reaction facilitating the later aqueous separation of the salt produced from the elemental material or alloy. This results in a substantial economic savings and simplifies the separation and recovery process.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention is to provide a method and system for producing metals or non metals or alloys thereof by an exothermic reaction between vapor phase halides and a liquid reducing metal in which the reducing metal is maintained in the vapor phase after the exothermic reaction in order to facilitate separation of the reaction products and the products made thereby.

Yet another object of the present invention is to provide an improved method and system for producing elemental materials or an alloy thereof by an exothermic reaction of a vapor halide of the elemental material or materials or halide mixtures thereof in a liquid reducing metal in which a sweep gas is used to separate the reducing metal in the vapor phase from the products of the exothermic reaction and the products made thereby.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of a system for practicing one method of the present invention;

FIG. 2 is a flow sheet of a representative example of the process as practiced in the system of Fig. 1 showing various flow rates and temperatures in the system;

FIG. 3 is a schematic representation of another system for practicing another embodiment of the present invention; and

FIG. 4 is a schematic representation of another embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to Figure 1 of the drawings, there is disclosed a system 10 for the practice of the invention. The system 10 includes a reactor 15 generally vertically displaced in this example in a drop tower vessel 16, the drop tower 16 having a central generally cylindrical portion 17, a dome top 18 and a frustoconical shaped bottom portion 19. A product outlet 20 is in communication with the frustoconical portion 19. The reactor 15 essentially consists of an apparatus illustrated in Figure 2 of U.S. patent no. 5,958,106 in which a tube through which liquid metal flows as a stream has inserted therein a halide(s) vapor so that the vapor halide(s) is introduced into the liquid reducing metal below the surface and is entirely surrounded by the liquid during the ensuing exothermic reaction.

A reducing metal inlet pipe 25 enters the reactor 15 near the top 18 and a vapor halide inlet 30 also enters the drop tower 16 near then top 18. However, it will be understood by a person of ordinary skill in the art that a variety of configurations of inlet conduits may be used without departing from the spirit and scope of the present invention.

As illustrated, there is an overhead exit line 35 through which vapor leaving reactor 15 can be drawn. The overhead exit line 35 leads to a condenser 37 where certain vapors are condensed and discharged through an outlet 38 and other vapor or gas, such as an inert gas, is pumped by a pump 40 through a heat exchanger 45 (see Fig. 2) and line 41 into the drop tower 16, as will be explained.

For purposes of illustration, in Figure 1 there is shown a reducing metal of sodium. It should be understood that sodium is only an example of reducing metals which may be used in the present invention. The present invention may be practiced with an alkali metal or mixtures of alkali metals or an alkaline earth metal or mixtures of alkaline earth metals or mixtures of alkali and alkaline earth metals. The preferred alkali metal is sodium because of its availability and cost. The preferred alkaline earth metal is magnesium for the same reason.

The preferred halide(s) to be used in the process of the present invention is a chloride, again because of availability and cost. The metals and non-metals which may be produced using the subject invention are set forth in Table 1 hereafter; the alloys of the metals and non-metals of Table 1 are made by introducing mixed halide vapor into the reducing metal.

TABLE 1

FEEDSTOCK	HEAT kJ/g
-	
TiCl ₄	-5
AlCl ₃	-5
SbCl ₃	-4
BeCl ₂	-6
BCl ₃	-8
TaCl ₆	-4
VCl ₄	-6
NbCl ₅	-5
MoF ₅	-10
GaCl ₃	-5
UF ₆	-4
ReF ₆	-8
ZrCl ₄	-4
SiCl ₄	-11

All of the elements in Table 1 result in an exothermic reaction with an alkali metal or alkaline earth metal to provide the halide(s) of the reducing metal and the metal or alloy of the halide introduced into the reducing metal. Ti is discussed only by way of example and is not meant to limit the invention. Because of the large heat of reaction, there has been the problem that the reaction products fuse into a

mass of material which is difficult to process, separate and purify. Discussions of the Kroll and Hunter processes appear in the patents referenced above.

The patents disclosing the Armstrong process show a method of producing a variety of metals and alloys and non-metals in which the heat of reaction resulting from the exothermic reaction is controlled by the use of excess liquid reducing metal and the reaction proceeds instantaneously by introducing the metal halide into a continuous phase of liquid reducing metal, otherwise described as a liquid continuum. The use of a subsurface reaction described in the Armstrong process has been an important differentiation between the batch processes and other suggested processes for making metals such as titanium and the process disclosed in the Armstrong et al. patents and application.

Nevertheless, the use of excess liquid reducing metal requires that the excess liquid metal be separated before the products can be separated. This is because the excess liquid reducing metal usually explosively reacts with water or is insoluble in water whereas the particulate products of the produced metal and the produced salt can be separated with water wash.

By way of example, when titanium tetrachloride in vapor form is injected into sodium liquid, an instantaneous reaction occurs in which titanium particles and sodium chloride particles are produced along with the heat of reaction. Excess sodium absorbs sufficient heat that the titanium particles do not sinter to form a solid mass of material. Rather, after the excess sodium is removed, such as by vacuum distillation suggested in the aforementioned Armstrong patents, the remaining particulate mixture of titanium and sodium chloride can be easily separated with water.

Nevertheless, vacuum distillation is expensive and it is preferred to find system and method that will permit the separation of the particulate reaction products of the reaction directly with water without the need of preliminary steps. This has been accomplished in the present invention by the discovery that by judiciously limiting the amount of excess reducing metal present, the boiling point of the produced salt will be the limiting temperature of the reaction and so long as the temperature of reaction products is maintained above the boiling point of the reducing metal and below the boiling point of the produced salt, any excess

reducing metal present will remain in the vapor phase which can be efficiently and inexpensively removed so that the particulates accumulating at the bottom 19 of the reaction vessel or drop tower 16 are entirely free of liquid reducing metal, thereby permitting the separation of the particulate reaction products with water, obviating the need for a separate vacuum distillation step.

As illustrated in Figure 2, the halide gases of the elemental material or alloy to be made such as titanium tetrachloride, come from a storage or supply 31. The titanium tetrachloride is fed, in one specific example only, at the rate indicated on Fig. 2, to a boiler 32 and from there via the inlet pipe 30 to the reactor 15. The sodium reducing metal is fed, in one specific example only at the rate indicated on Fig. 2, from a storage container 26 through an inlet line 25 to the reactor 15. As before stated, the liquid sodium flows in the specific example as indicated on Fig. 2 in a 50% excess quantity of the stoichiometric amount needed to convert the titanium tetrachloride to titanium metal and as indicated in Fig. 2 at a temperature of 200°C at which the sodium is liquid.

In the reactor 15, as previously taught in the Armstrong patents and application, the continuous liquid phase of sodium is established into which the titanium tetrachloride vapor is introduced and instantaneously causes an exothermic reaction to occur producing large quantities of heat, and particulates of titanium metal and sodium chloride. The boiling point of sodium chloride is 1465°C and becomes the upper limit of the temperature of the reaction products. The boiling point of sodium is 892°C and is the lower limit of the temperature of the reaction products to ensure that all excess sodium remains in the vapor phase until separation from the particulate reaction products. A choke flow nozzle also known as a critical flow nozzle is well known and used in the line transmitting halide vapor into the liquid reducing metal, all as previously disclosed in the '761 and '106 patents. It is critical for the present invention that the temperature of the reaction products as well as the excess reducing metal be maintained between the boiling point of the reducing metal, in this case sodium, and the boiling point of the salt produced, in this case sodium chloride.

The vapors exiting the reactor 15 are drawn through exit line 35 along with an inert sweep gas introduced through the inert gas inlet 41. The inert gas, in this

example argon, may be introduced at a temperature of about 200°C, substantially lower than the temperature of the reaction products which exit the tower 16 at 800°C. The argon sweep gas flows, in the example illustrated in Fig. 1, countercurrently to the direction of flow of the particulate reaction products. The sodium vapor is swept by the argon into the outlet 35 along with whatever product fines are entrained in the gas stream comprised of argon and sodium vapor at about 900°C and transmitted to the condenser 37. In the condenser 37, as shown in Fig. 2, heat exchange occurs in which the sodium vapor is cooled to a liquid at about 400°C and recycled to the sodium feed or inlet 25 via line 38 and the argon is cooled from 400°C, the temperature at which it exits the condenser 37 by a cooler 45 to the 200°C temperature at which it is recycled as shown in Fig. 2. It is seen therefore, that the inert gas preferably flows in a closed loop and continuously recirculates as long as the process is operational. The product fines present in the condenser 37 will be removed by filters (not shown) in both the sodium recycling line 38 and in the line 39 exiting the condenser 37 with the inert gas.

As the inert gas moves upwardly through the vessel or drop tower 16, there is contact between the colder inert gas and the reaction particulates which are at a higher temperature. As seen from Fig. 2, the sodium vapor exits the drop tower 16 at a temperature of about 900°C while the particulate product exits the reactor 15 at a temperature not greater than 1465°C. After being cooled by contact with the argon gas, the particulate product, in this example, is at a temperature of about 800°C at the exit or product outlet 20. The product 20 which leaves the vessel 16 at about 800°C enters a cooler 21, see Fig. 2, to exit therefrom at 50°C.

Thereafter, the product is introduced through line 22 to a water wash 50 in which water is introduced into a container through a line 51 and brine exits from the water wash 50 via line 53. The titanium particulates exit from the water wash through a line 52 for drying and further processing.

It should be understood that although titanium is shown to be the product in Figs. 1 and 2 any of the elements or alloys thereof listed in Table 1 may be produced by the method of the present invention. The most commercially important metals at the present time are titanium and zirconium and their alloys. The most preferred titanium alloy for defense use is 6% aluminum, 4% vanadium,

the balance substantially titanium. This alloy known as 6:4 titanium is used in aircraft industry, aerospace and defense. Zirconium and its alloys are important metals in nuclear reactor technology. Other uses are in chemical process equipment.

The preferred reducing metals at the present time because of cost and availability are sodium of the alkali metals and magnesium of the alkaline earth metals. The boiling point of magnesium chloride is 1418°C and the boiling point of magnesium is 1107°C. Therefore, if magnesium were to be used rather than sodium as the reducing metal, then preferably the product temperature would be maintained between the boiling point of magnesium and the boiling point of magnesium chloride, if the chloride salt of the metal or alloy to be produced were to be used. The chlorides are preferred because of cost and availability.

One of the significant features of the present invention is the complete separation of reducing metal from the particulate reaction products as the reaction products leave the reactor 15 thereby providing at the bottom of the drop tower 16 a sodium free or reducing metal-free product which may then be separated with water in an inexpensive and uncomplicated process. If liquid sodium or other reducing metal is trapped within the product particulates, it must be removed prior to washing. Accordingly, the invention as described is a significant advance with respect to the separation of the metal or alloy particulates after production disclosed in the aforementioned Armstrong et al. patents and application.

Referring to Figure 3, there is disclosed another embodiment of the present invention system 110 which includes a reactor 115 disposed within a drop tower 116 having a cylindrical center portion 117, a dome topped portion 118 and a frustoconical bottom portion 119 connected to a product outlet 120. A plurality of cooling coils 121 are positioned around the frustoconical portion 119 of the drop tower 116 for a purpose to be explained.

As in the system 10 shown in Figs. 1 and 2, there is a metal halide inlet 130 and a reducing metal inlet 125 in communication with the reactor 115 disposed within the drop tower 116. An overhead exit line 135 leads from the dome top portion 118 of the drop tower 116 to a condenser 137 in fluid communication with a pump 140. A liquid reducing metal and product fine outlet 138 is also provided

from the condenser 137.

In operation, the system 110 is similar to the system 10 in that a liquid reducing metal, for instance sodium or magnesium, is introduced via inlet 125 from a supply thereof at a temperature above the melting point of the metal, (the melting point of sodium is 97.8°C and for Mg is 650°C) such as 200°C for sodium and 700°C for Mg. The vapor halide of the metal or alloy to be produced, in this case titanium tetrachloride, is introduced from the boiler at a temperature of about 200°C to be injected as previously discussed into a liquid so that the entire reaction occurs instantaneously and is subsurface. The products coming from the reactor 115 include particulate metal or alloy, excess reducing metal in vapor form and particulate salt of the reducing metal. In the system 110, there is no sweep gas but the drop tower 116 is operated at a pressure slightly in excess of 1 atmosphere and this by itself or optionally in combination with the vacuum pump 140 causes the reducing metal vapor leaving the reactor 115 to be removed from the drop tower 116 via the line 135. A certain amount of product fines may also be swept away with the reducing metal vapor during transportation from the drop tower 116 through the condenser 137 and the liquid reducing metal outlet 138. A filter (not shown) can be used to separate any fines from the liquid reducing metal which is thereafter recycled to the inlet 125.

Cooling coils 121 are provided, as illustrated on the bottom 119 of the drop tower 116. A variety of methods may be used to cool the drop tower 116 to reduce the temperature of the product leaving the drop tower 116 through the product outlet 120. As illustrated in Fig. 3, a plurality of cooling coils 121 may be used or alternatively, a variety of other means such as heat exchange fluids in contact with the container or heat exchange medium within the drop tower 116. What is important is that the product be cooled but not the reducing metal vapor so that the excess reducing metal in vapor phase can be entirely separated from the product prior to the time that the product exits the drop tower 116 through the product outlet 120.

In the example illustrated, titanium tetrachloride and liquid sodium enter the reactor 115 at a temperature of about 200°C and titanium and salt exit the drop tower 116 through product outlet 120 at about 700°C. The excess sodium vapor

leaves the dome 118 of the drop tower 116 at approximately 900°C and thereafter is cooled in the condenser 137 to form liquid sodium (below 892°C) which is then recycled to inlet 125. In this manner, dry product is produced, free of liquid reducing metal, without the need of a sweep gas.

Referring now to Figure 4, there is disclosed another embodiment of the invention. A system 210 in which like parts are numbered in the 200 series as opposed to the 100 series. Operation of the system 210 is similar to the operation of the system 10 but in the system 210 an inert sweep gas flows co-currently with the product as opposed to the countercurrent flow as illustrated in system 10 and Figures 1 and 2. In the system 210 illustrated in Fig. 4, the gas flow is reversed in comparison to the system 10. In the system 210, the sweep gas such as argon, the reducing metal vapor such as sodium vapor and the product of titanium particles and sodium chloride exit through the outlet 220 into a demister or filter 250. The demister or filter 250 is in fluid communication with a condenser 237 and a pump 240 so that the sodium vapor and the argon along with whatever fines come through the demister or filter 250 are transported via a conduit 252 to the condenser 237. In the condenser 237, the sodium is cooled and condensed to a liquid, the fines are separated while the argon or inert gas is cooled and recycled via the pump 240 in line 235 to the drop tower 216. The other apparatus of the system 210 bear numbers in the 200 series that are identical to the numbers in the system 10 and 100 and represent the same part functioning in the same or similar manner.

It is seen that the present invention can be practiced with a sweep gas that is either countercurrent or co-current with the reaction products of the exothermic reaction between the halide and the reducing metal or without a sweep gas. An important aspect of the invention is the separation of the reducing metal in vapor phase prior to the separation of the produced metal and the produced salt. When using sodium as the reducing metal, the preferred excess sodium, that is the sodium over an above the stoichiometric amount necessary to reduce the metal halide, is in the range of from about 25% to about 125% by weight. More specifically, it is preferred that the excess sodium with respect to the stoichiometric amount required for reduction of the halide of the elemental material mixtures is

from about 25% to about 85% by weight. When magnesium is used as the reducing metal as opposed to sodium, then the excess of magnesium in the liquid phase over and above the stoichiometric amount required for the reduction of the halide is in the range of from about 5% to about 150% by weight. More specifically, the preferred excess magnesium is in the range of from about 5% by weight to about 75% by weight with respect to the stoichiometric amount required for the reduction of the halide. More specifically, it is preferred, but not required, that the liquid reducing metal be flowing in a conduit as illustrated in Fig. 2 of the '106 patent previously referred to and incorporated herein by reference.

Various alloys have been made using the process of the present invention. For instance, titanium alloys including aluminum and vanadium have been made by introducing predetermined amounts of aluminum chloride and vanadium chloride and titanium chloride to a boiler or manifold and the mixed halides introduced into liquid reducing metal. For instance, grade 5 titanium alloy is 6% aluminum and 4% vanadium. Grade 6 titanium alloy is 5% aluminum and 2.5% tin. Grade 7 titanium is unalloyed titanium and paladium. Grade 9 titanium is titanium alloy containing 3% aluminum and 2.5% vanadium. Other titanium alloys include molybdenum and nickel and all these alloys may be made by the present invention.

In one specific example of the invention, adjustment was made to the sodium flow and temperature by controlling the power to the heater and pump to obtain an inlet temperature of 200°C at a flow of 3.4 kg/min. This provided a production rate of 1.8 kg/min of titanium powder and required a feed of 6.9 kg/min of titanium tetrachloride gas for a stoichiometric reaction. The desired feed rate of titanium tetrachloride is obtained by controlling the pressure of the titanium tetrachloride vapor upstream of a critical flow nozzle by adjusting the power to the titanium tetrachloride boiler. At this stoichiometric ratio, the adiabatic reaction temperature (1465°C) is the boiling temperature of the reaction product of sodium chloride, and a heat balance calculation shows that about 66% of the sodium chloride is vaporized.

$$0 = \Delta H_{\text{reaction}} - \Delta H_{\text{products}} + \Delta H_{\text{reactants}}$$

$$\Delta H_{\text{products}} = C_{p_{\text{Ti}}}(T_a - 293\text{K}) + 4(\Delta H_{f_{\text{NaCl}}} + x\Delta H_{v_{\text{NaCl}}} + (T_a - T_{m_{\text{NaCl}}})C_{p_{\text{NaCl}}} + (T_{m_{\text{NaCl}}} - 293\text{K})C_{p_{\text{NaCl}s}})$$

$$\Delta H_{\text{reactants}} = \Delta H_{v_{\text{TiCl}_4}} + (T_{\text{in}} - 293\text{K})C_{p_{\text{TiCl}_4}} + 4(\Delta H_{f_{\text{Na}}} + (T_{\text{in}} - T_{m_{\text{Na}}})C_{p_{\text{Na}}} + (T_{m_{\text{Na}}} - 293\text{K})C_{p_{\text{Na}s}})$$

where

$\Delta H_{\text{reaction}} = -841.5 \text{ kJ/mole}$	heat of reaction
$C_{p_{\text{Ti}}} = 28.0 \text{ J/moleK}$	solid titanium heat capacity
$T_a = 1738\text{K}$	adiabatic reaction temperature
$\Delta H_{f_{\text{NaCl}}} = 28.0 \text{ kJ/mole}$	sodium chloride specific heat
$x = \text{fraction of NaCl vaporized}$	sodium chloride vapor fraction
$\Delta H_{v_{\text{NaCl}}} = 171.0 \text{ kJ/mole}$	sodium chloride heat of vaporization
$T_{m_{\text{NaCl}}} = 1074\text{K}$	sodium chloride melting temperature
$C_{p_{\text{NaCl}}} = 55.3 \text{ J/moleK}$	liquid sodium chloride specific heat
$C_{p_{\text{NaCl}s}} = 58.2 \text{ J/moleK}$	solid sodium chloride specific heat
$\Delta H_{v_{\text{TiCl}_4}} = 35.8 \text{ kJ/mole}$	titanium tetrachloride heat of vaporization
$T_{\text{in}} = 473\text{K}$	sodium inlet temperature
$C_{p_{\text{TiCl}_4}} = 145.2 \text{ J/moleK}$	gaseous titanium tetrachloride specific heat
$\Delta H_{f_{\text{Na}}} = 2.6 \text{ kJ/mole}$	sodium heat of fusion
$T_{m_{\text{Na}}} = 371\text{K}$	sodium melting temperature
$C_{p_{\text{Na}}} = 31.4 \text{ J/moleK}$	liquid sodium specific heat
$C_{p_{\text{Na}s}} = 28.2 \text{ J/moleK}$	solid sodium specific heat

Increasing the sodium flow rate to 6.3 kg/min at the same titanium tetrachloride rate will still give an adiabatic reaction temperature of 1465°C but there will be about 0% sodium chloride vapor present in the reaction zone. Increasing the sodium flow rate above this level will cause a reduction in the adiabatic reaction temperature but at least to a flow of 7.6 kg/min, the reaction temperature will remain above the normal boiling temperature of sodium (883°C) and all of the sodium will leave the reaction zone as vapor.

Accordingly, there has been disclosed an improved process for making and separating the products of the Armstrong process resulting from the exothermic

reaction of a metal halide with a reducing metal. A wide variety of important metals and alloys can be made by the Armstrong process and separated according to this invention.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of producing an elemental material or an alloy thereof from a halide of the elemental material or halide mixtures comprising introducing the vapor halide of an elemental material or halide mixtures thereof into a liquid phase of a reducing metal of an alkali metal or alkaline earth metal or mixtures thereof present in excess of the amount needed to reduce the halide vapor to the elemental material or alloy resulting in an exothermic reaction between the vapor halide and the liquid reducing metal producing particulate elemental material or alloy thereof and the halide salt of the reducing metal and sufficient heat to vaporize substantially all the excess reducing metal, and separating the vapor of the reducing metal from the particulate elemental material or alloy thereof.
2. The method of claim 1, wherein the elemental material or alloy is one or more of Ti, Al, Sb, Be, B, Ga, Mo, Nb, Ta, V, Zr, U, Re, Si, Os, Ir and mixtures thereof.
3. The method of claim 2, wherein the reducing metal is an alkali metal.
4. The method of claim 3, wherein the reducing metal is Na.
5. The method of claim 3, wherein the liquid phase is Na present in excess of the stoichiometric amount required for the reduction of the halide of the elemental material or mixtures in the range of from about 25% to 125% by weight.
6. The method or claim 3, wherein the liquid phase is Na present in excess of the stoichiometric amount required for the reduction of the halide of the elemental material or mixtures in the range of from about 25% to about 85% by weight.
7. The method of claim 3, wherein the halide is a chloride and the liquid phase is Na present in excess of the stoichiometric amount required for the reduction of the chloride of the elemental material or mixtures in the range of from about 25% to 125% by weight.
8. The method of claim 7, wherein the elemental material is titanium and the Na is present in excess of the stoichiometric amount required for the reduction of the chloride of the elemental material or mixtures in the range of from about 25% to about 85% by weight.

9. The method of claim 7, wherein the elemental material or an alloy thereof includes titanium and the Na is flowing.

10. The method of claim 2, wherein the reducing metal is an alkaline earth metal.

11. The method of claim 10, wherein the reducing metal is Mg.

12. The method of claim 10, wherein the halide is a chloride and the liquid phase is Mg present in excess of the stoichiometric amount required for the reduction of the halide of the elemental material or mixtures in the range of from about 5% to 150% by weight.

13. The method of claim 10, wherein the liquid phase is Mg present in excess of the stoichiometric amount required for the reduction of the halide of the elemental material or mixtures in the range of from about 5% to about 75% by weight.

14. The method of claim 12, wherein the elemental material or alloy thereof includes titanium and the Mg is flowing.

15. The method of claim 2, wherein the alloy is substantially Ti and Al and V and is formed by introducing the chlorides thereof as vapor into a liquid phase of a reducing metal.

16. The method of claim 2, wherein the reducing metal vapor is separated from the particulate reaction products with an inert sweep gas.

17. The method of claim 16, wherein the reducing metal is Na, the inert sweep gas is Ar and the alloy is Ti - 6% by weight Al - 4% by weight V.

18. The method of claim 16, wherein the reducing metal is Mg, the inert sweep gas is Ar and the alloy is Ti-6% by weight Al - 4% by weight V.

19. The method of claim 1, wherein the temperature of the particulate elemental material or alloy thereof is maintained at or below the boiling point of the halide salt of the alkali metal or alkaline earth metal.

20. The method of claim 16, wherein the inert sweep gas flows countercurrently to the particulate reaction products.

21. The method of claim 16, wherein the inert sweep gas flows concurrently with the particulate reaction products; and filtering the particulate reaction

products from the sweep gas and the reducing metal vapor.

22. The method of claim 1, wherein the reducing metal vapor is separated from the particulate reaction products by condensing the vapor at a location remote from the reaction products.

23. The method of claim 1, wherein the particulate reaction products are cooled before separation of the halide salt from elemental material or alloy thereof.

24. The method of claim 1, wherein the particulate elemental material or alloy thereof is cooled below the sintering temperature before the particulate material or alloy thereof agglomerates.

25. The method of claim 1, wherein formation of the particulate elemental material or alloy thereof is at atmospheric pressure and the separation of the reducing metal vapor is at or below atmospheric pressure.

26. The method of claim 1, wherein the temperature of the particulate reaction products does not exceed the boiling point of the halide salt produced.

27. The method of claim 26, wherein the temperature of the particulate reaction products is maintained at or above the boiling point of the reducing metal until the reducing metal vapor is entirely separated from the particulate reaction products.

28. A method of producing Ti or a Ti alloy comprising introducing a Ti chloride vapor or a mixture of Ti chloride and other chloride vapors into a liquid continuum of a reducing metal of an alkali metal or alkaline earth metal or mixtures thereof initiating an exothermic reaction to form particulate Ti or Ti alloy and a chloride salt of the reducing metal, the reducing metal being present in excess of the stoichiometric amount required to react with the Ti chloride or mixture of Ti chloride and other chloride vapor, the exothermic reaction producing heat sufficient to vaporize substantially all the excess reducing metal, and separating the reducing metal vapor from the particulate Ti or Ti alloy and the chloride salt of the reducing metal.

29. The method of claim 28, wherein the formation of particulate Ti or alloy thereof and separation of reducing metal vapor is at substantially atmospheric pressure.

30. The method of claim 28, wherein the formation of particulate Ti or alloy thereof is at substantially atmospheric pressure and the separation of the reducing metal is in part at less than atmospheric pressure.

31. The method of claim 28, wherein the reducing metal is Na and the temperature of the particulate Ti or Ti alloy is maintained at or below the boiling point of NaCl.

32. The method of claim 28, wherein the reducing metal is Mg and the temperature of the particulate Ti or Ti alloy is maintained at or below the boiling point of MgCl_2 .

33. The method of claim 28, wherein reducing metal vapor is separated from the particulate reaction products with an inert sweep gas.

34. The method of claim 28, wherein the particulate reaction products are cooled with an inert sweep gas.

35. The method of claim 28, wherein the chloride vapor is introduced into a flowing stream of reducing metal.

36. The method of claim 35, wherein the particulate Ti or Ti alloy is cooled below the sintering temperature thereof before the particulate Ti or Ti alloy agglomerates.

37. The method of claim 28, wherein the reducing metal vaporized during the formation of the reaction products is maintained in the vapor phase and is separated from the reaction products by condensing the reducing metal thereby creating an area of reduced pressure into which a reducing metal vapor is drawn.

38. A method of producing Ti or a Ti alloy, comprising producing Ti or Ti alloy particulates in an exothermic reaction by introducing Ti chloride vapor or a mixture of Ti chloride and other chloride vapor into a flowing stream of liquid reducing metal of an alkali metal or an alkali earth metal or mixtures thereof, the reducing metal being present in an amount in excess of the stoichiometric amount required to react all of the Ti chloride or mixtures of Ti chloride and other chloride vapor, the heat of reaction vaporizing the excess liquid reducing metal such that substantially no reducing metal is present as a liquid after the reaction, the Ti or Ti alloy particulates moving in a first direction through a vessel, establishing a flow of inert gas to contact the Ti or Ti alloy particulates to separate the substantially all

18_f

the excess reducing metal vapor from the Ti or Ti alloy particulates, and removing the Ti or Ti alloy particulates from the vessel.

39. The method of claim 38, wherein first direction is generally downwardly and the inert gas flows generally upwardly.

40. The method of claim 38, wherein a Ti alloy is produced by mixing TiCl_4 and AlCl_3 .

41. The method of claim 38, wherein a Ti alloy is produced by mixing TiCl_4 and a V chloride.

42. The method of claim 38, wherein a Ti alloy is produced by mixing chlorides of Ti and Al and V in a predetermined weight ratio and thereafter reducing the mixture to an alloy of Ti and Al and V.

43. The method of claim 43, wherein the Ti and Al and V alloy includes about 6% by weight Al and about 4% by weight V, the balance being substantially Ti.

44. The method of claim 43, wherein the reducing metal is Na and the inert gas is Ar.

45. The method of claim 38, wherein the inert gas cools the Ti or Ti alloy particulates.

46. A method of producing Ti or a Ti alloy, comprising producing Ti or Ti alloy particulates from an exothermic reaction by introducing Ti chloride vapor or a mixture of Ti chloride and other chloride vapor into a flowing stream of liquid reducing metal of Na or Mg, the reducing metal being present in an amount in excess of the stoichiometric amount required to react all of the Ti chloride or mixtures of Ti chloride and other chloride vapor, the heat of reaction vaporizing substantially all the excess Na or Mg such that substantially no Na or Mg is present as a liquid after the reaction, the Ti or Ti alloy particulates moving downwardly through a vessel, establishing a flow of inert gas upwardly through the vessel for cooling the particulates and separating the excess Na or Mg vapor from the particulates, and removing the Ti or Ti alloy particulates from the vessel.

47. The method of claim 46, wherein the reducing metal is Na.

48. The method of claim 47, wherein the liquid Na is present in an amount of about 25% to 85% by weight in excess of the stoichiometric amount required for the reduction of the Ti chloride or mixtures of Ti chloride and other chloride vapor.

49. The method of claim 46, wherein the reducing metal is Mg.

50. The method of claim 49, wherein the Mg is present in an amount of about 5% to about 75% by weight in excess of the stoichiometric amount required for the reduction of the Ti chloride or mixture of Ti chloride and other chloride vapor.

51. A method of producing Ti particles substantially free of Na, comprising introducing TiCl_4 vapor into a liquid continuum of Na to produce Ti particles and NaCl and heat in an exothermic reaction, the Na being present in an amount in the range of about 25% to 125% by weight in excess of the stoichiometric amount of Na needed to reduce all the TiCl_4 to Ti, the temperature of the reaction products of Ti and NaCl particles being maintained at less than about the boiling point of NaCl and greater than the boiling point of Na after the chemical reaction of TiCl_4 and Na such that substantially all excess Na is in the vapor phase, the Na vapor being separated from the reaction products of NaCl and Ti with a moving gas, and thereafter separating the Ti from the NaCl.

52. The method of claim 51, wherein one or more other chlorides are mixed with the TiCl_4 prior to contact with the reducing metal to produce particles of Ti alloy.

53. The method of claim 52, wherein the chlorides mixed with TiCl_4 are Al chloride and V chloride.

54. The method of claim 53, wherein the alloy is about 6% by weight Al and about 4% by weight V and the balance substantially all Ti.

55. The method of claim 51, wherein the process is conducted at atmospheric pressure.

56. The method of claim 51, wherein the moving gas is inert with respect to Na and Ti and NaCl.

57. The method of claim 56, wherein the inert gas is Argon.

58. The method of claim 57, wherein the Ti is separated from the NaCl by dissolving the NaCl in water.

59. The method of claim 58, wherein the Na is present in the range of from about 25% by weight to about 85% by weight in excess of the stoichiometric amount needed to reduce the TiCl_4 to Ti.

60. A system for the production of Ti or a Ti alloy, comprising a reactor for introducing a Ti halide vapor or a mixture of Ti halide and other metal halide vapor into a continuous phase of a liquid reducing metal to initiate an exothermic reaction reducing the halide vapor to produce reaction products of Ti or Ti alloy particulates and the halide of the reducing metal, the reducing metal being present in an amount greater than the stoichiometric amount needed to reduce the halide or halides but only in the amount which will substantially vaporize during the reaction, such that substantially no liquid reducing metal is present in the reaction products, a chamber wherein the reaction products are separated from the reducing metal vapor and the reaction products are cooled, and a separator in which the halides of the reducing metal are separated from the Ti or Ti alloy particulates by washing with water.

61. The system of claim 60, wherein said reactor is positioned in said chamber and further including a condenser in communication with said vessel for condensing the vapor of the excess reducing metal to a liquid and recycle equipment to recycle excess condensed reducing metal to the reactor.

62. The system of claim 61, wherein the condenser is in communication with a pump to operate at a lower pressure than the reactor, and further including heat exchange equipment in thermodynamic relationship with at least a portion of said chamber to cool the reaction products.

63. The system of claim 60, and further including a gas inlet and a gas outlet in communication with said chamber to establish a sweep gas flow path for a sweep gas to flow through the chamber to contact the reaction products to cool same.

64. The system of claim 63, wherein the sweep gas is Ar and exits the chamber with the excess reducing metal vapor, and further including a condenser for condensing the reducing metal vapor to a liquid for recycle to the reactor

thereby separating the reducing metal from the Ar and a heat exchanger for cooling the Ar and recycling the cooled Ar to the chamber.

65. The system of claim 64, wherein the sweep gas flow is countercurrent with respect to the reaction products to exit the chamber near the top thereof.

66. The system of claim 64, wherein the sweep gas flow is co-current with respect to the reaction products to exit the chamber near the bottom thereof.

67. The system of claim 66, wherein the product exits the chamber as a liquid.

68. The system of claim 64, wherein the halides are chlorides and the reducing metal is Na present in the range of from about 25% to about 85% by weight in excess of the stoichiometric amount needed to reduce the Ti chloride and/or the mixture of chloride vapor.

69. The system of claim 61, and further including a boiler for heating the Ti chloride or mixtures of Ti chloride and other chlorides before introduction to the reactor.

70. The system of claim 60, wherein the chamber is positioned generally vertically.

71. A method of producing an elemental material or an alloy thereof from a halide of the elemental material or halide mixtures comprising introducing the vapor halide of an elemental material or halide mixtures thereof into a liquid phase of a reducing metal of an alkali metal or alkaline earth metal or mixtures thereof present in excess of the amount needed to reduce the halide vapor to the elemental material or alloy resulting in an exothermic reaction producing particulate elemental material or alloy thereof and the halide salt of the alkali metal or alkaline earth metal or mixtures thereof, the temperature of the reaction products of the particulate elemental material or alloy thereof and the halide salt of the reducing metal being maintained at less than the boiling point of the halide salt of the reducing metal and greater than the boiling point of the reducing metal until substantially all excess reducing metal is vaporized, and separating the reducing metal vapor from the particulate elemental material or alloy thereof.

72. The method of claim 71, wherein the elemental material or alloy is one or more of Ti, Al, Sb, Be, B, Ga, Mo, Nb, Si, Ta, Zr, V and mixtures thereof.

73. The method of claim 72, wherein the elemental material is Ti or Zr or alloys thereof and the reducing metal is Na or Mg and the halide is a chloride.

74. The method of claim 73, wherein the reducing metal is Na present in the liquid phase in the range of from about 25% to 125% by weight in excess of the stoichiometric amount required for the reduction.

75. The method of claim 73, wherein the reducing metal is Mg present in the liquid phase in the range of from about 5% to 150% by weight in excess of the stoichiometric amount required for the reduction.

76. A method of producing an elemental material or an alloy thereof from a chloride of the elemental material or chloride mixtures comprising introducing the vapor chloride of an elemental material or chloride mixtures thereof into a flowing liquid phase of a reducing metal of sodium or magnesium, sodium if present in the liquid phase is in the range of from about 25% by weight to about 125% by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor or magnesium if present in the liquid phase is in the range of from about 5% by weight to about 150% by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor to the elemental material or alloy resulting in an exothermic reaction producing particulate elemental material or alloy thereof and sodium chloride or magnesium chloride and sufficient heat to vaporize substantially all the excess sodium or magnesium, and separating the sodium or magnesium vapor from the particulate elemental material or alloy thereof and sodium chloride or magnesium chloride with an inert sweep gas.

77. A method of producing an elemental material or an alloy thereof from a chloride of the elemental material or chloride mixtures comprising introducing the vapor chloride of an elemental material or chloride mixtures thereof into a flowing liquid phase of a reducing metal of sodium or magnesium, sodium if present in the liquid phase is not more than by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor or magnesium if present in the liquid phase is not more than about 75% by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor to the elemental material or

alloy resulting in an exothermic reaction producing particulate elemental material or alloy thereof and sodium chloride or magnesium chloride and sufficient heat to vaporize substantially all the excess sodium or magnesium, and separating the sodium or magnesium vapor from the particulate elemental material or alloy thereof and sodium chloride or magnesium chloride with an argon sweep gas.

78. A method of producing Ti or Zr or alloys thereof from a chloride of Ti or Zr or chloride mixtures comprising introducing the Ti or Zr vapor chloride or chloride mixtures thereof into a flowing liquid phase of a reducing metal of sodium or magnesium, sodium if present in the liquid phase is in the range of from about 25% by weight to about 125% by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor or magnesium if present in the liquid phase is in the range of from about 5% by weight to about 150% by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor to cause an exothermic reaction producing particulate Ti or Zr or alloys thereof and sodium chloride or magnesium chloride and sufficient heat to vaporize substantially all the excess sodium or magnesium while maintaining the temperature of the reaction products between the boiling point of the reducing metal and the boiling point of the salt produced, separating the sodium or magnesium vapor from the particulate Ti or Zr or alloys thereof and sodium chloride or magnesium chloride with an inert sweep gas of argon, and separating the particulate Ti or Zr or alloys thereof from the sodium chloride or magnesium chloride with water.

79. A method of producing an elemental material or an alloy thereof from a chloride of the elemental material or chloride mixtures comprising introducing the vapor chloride of an elemental material or chloride mixtures thereof into a flowing liquid phase of a reducing metal of sodium or magnesium, sodium if present in the liquid phase is in the range of from about 25% by weight to 125% by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor or magnesium if present in the liquid phase is in the range of from about 5% by weight to 150% by weight in excess of the stoichiometric amount required for the reduction of the chloride vapor to the elemental material or alloy resulting in an exothermic reaction producing particulate elemental material or alloy thereof and sodium chloride or magnesium chloride and sufficient heat to vaporize substantially

all the excess sodium or magnesium, and separating the sodium or magnesium vapor from the particulate elemental material or alloy thereof and sodium chloride or magnesium chloride with an inert sweep gas.

- 80. A product made by the method of claim 1.
- 81. A product made by the method of claim 28.
- 82. A product made by the method of claim 38.
- 83. A product made by the method of claim 51.
- 84. A product made by the method of claim 79.

1/4

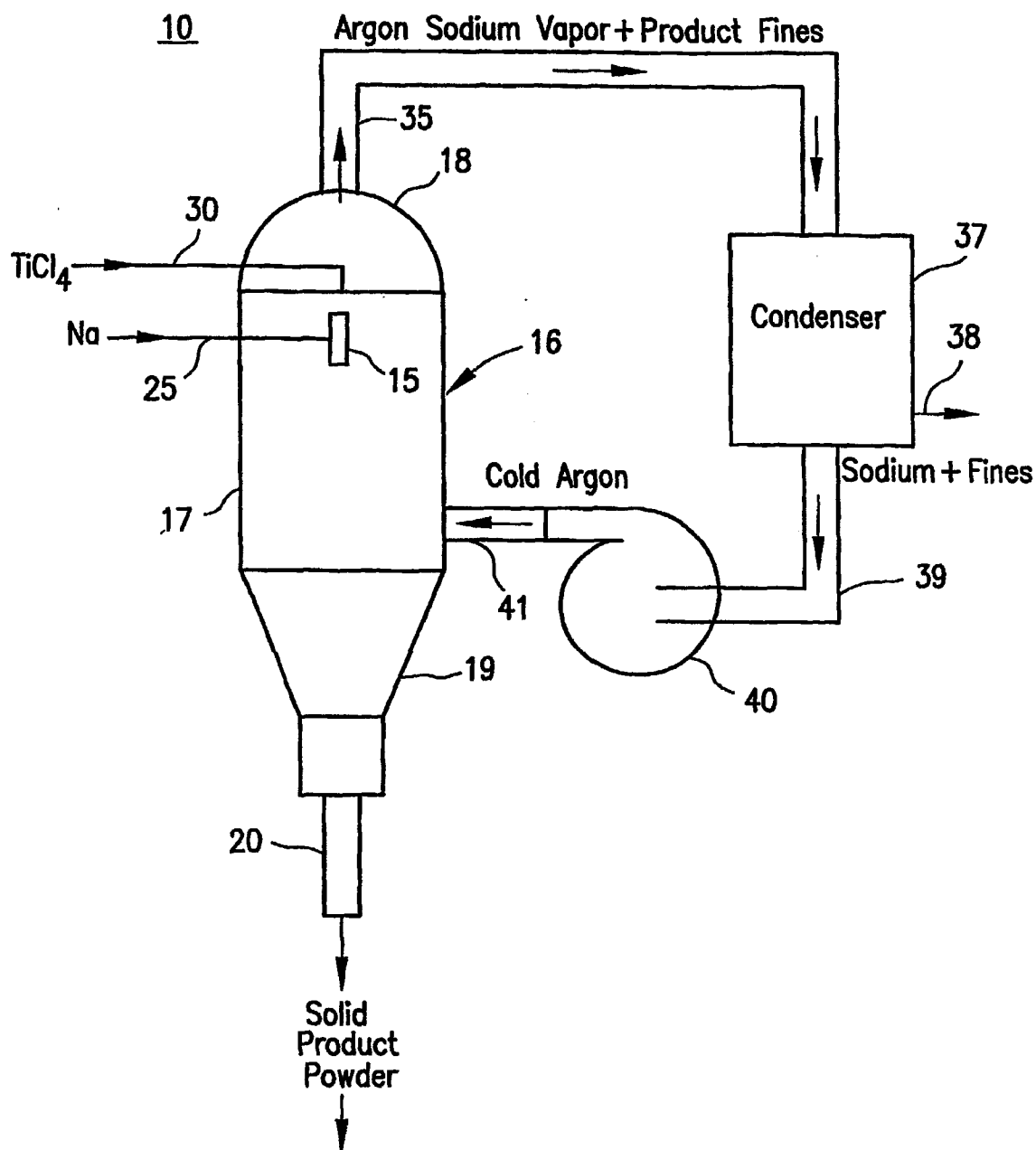


FIG. 1

2/4

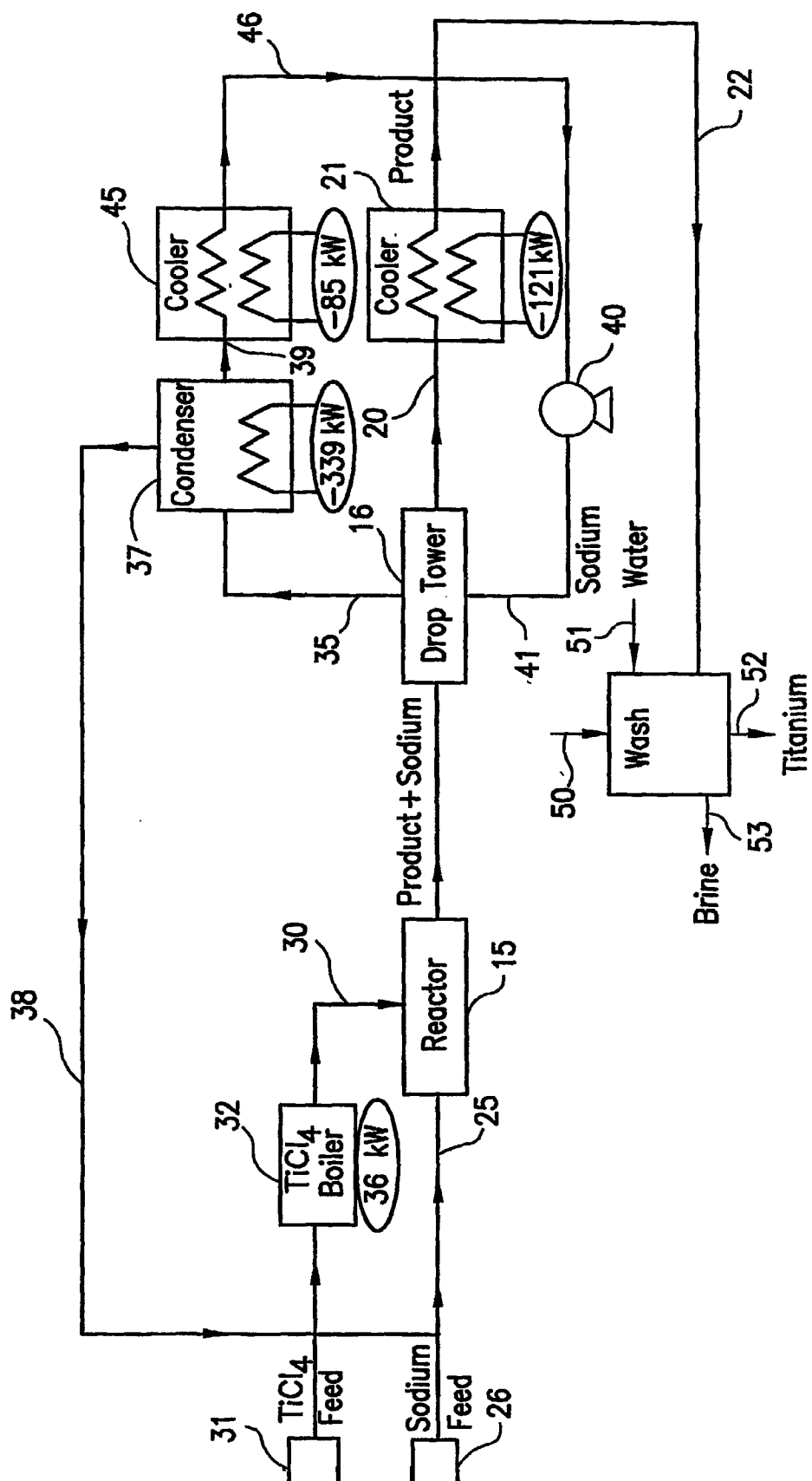


FIG. 2

3/4

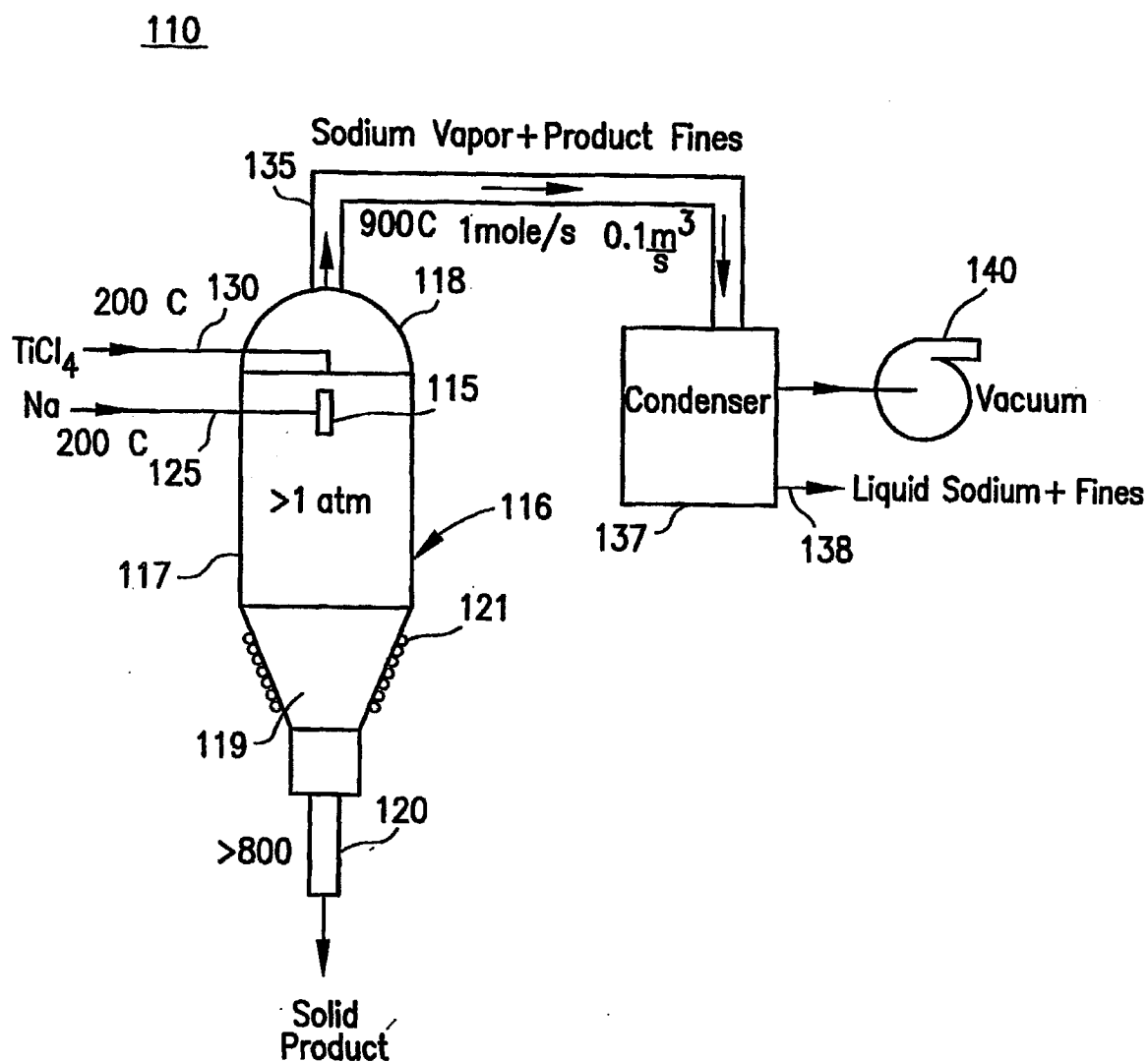


FIG. 3

4/4

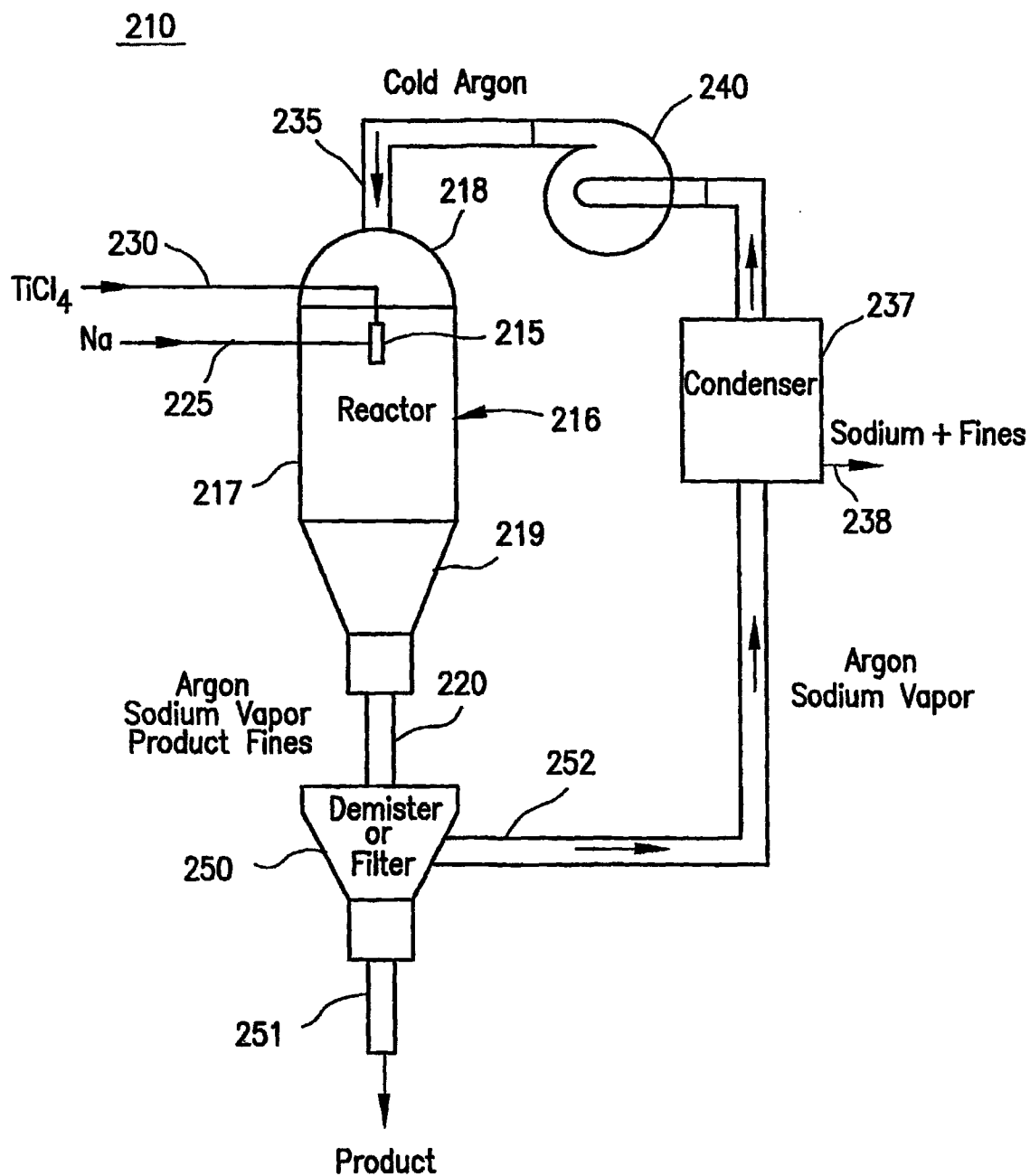


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/27651

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C22B34/12 B22F9/28 C22C1/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C22B B22F C22C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the International search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, COMPENDEX, INSPEC		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 958 106 A (ANDERSON RICHARD PAUL ET AL) 28 September 1999 (1999-09-28) cited in the application	1
X	claim 1; figures	60-70,80
A	US 2 647 826 A (FERNANDO JORDAN JAMES) 4 August 1953 (1953-08-04)	1
X	claim 1; figures	60,80
A	GB 722 184 A (DAVID HARRY PICKARD; JOSEPH PEPP0 LEVY; LIONEL PICKARD) 19 January 1955 (1955-01-19)	1
X	claim 1; figure 1	60,80
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the International search 20 November 2003		Date of mailing of the International search report 02/12/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Alvazzi Delfrate, M

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/27651

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 28-59, 71-79, 81-84
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 28-59, 71-79, 81-84

In view of the large number (10 independent method claims, one independent device claim and 5 independent product claims) and also the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear and concise, namely the method according to claim 1 (with appendant claims 2-27), the device according to claim 60 (with appendant claims 61-70) and the product according to claim 80. The remaining claims 28-59, 71-79, 81-84 will not be searched.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No
PCT/US 03/27651

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5958106	A	28-09-1999	US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2002005090 A1	17-01-2002
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A ,B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
			RU 2152449 C1	10-07-2000
			WO 9604407 A1	15-02-1996
<hr/>				
US 2647826	A	04-08-1953	NONE	
<hr/>				
GB 722184	A	19-01-1955	NONE	
<hr/>				

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number
WO 2004/033737 A1

(51) International Patent Classification⁷: **C22B 34/12**,
B22F 9/28, C22C 1/04

(74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar, 300
South Wacker Drive, Suite 3000, Chicago, IL 60606 (US).

(21) International Application Number:
PCT/US2003/027659

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date:
3 September 2003 (03.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/416,611 7 October 2002 (07.10.2002) US

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **INTER-
NATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

(72) Inventors; and

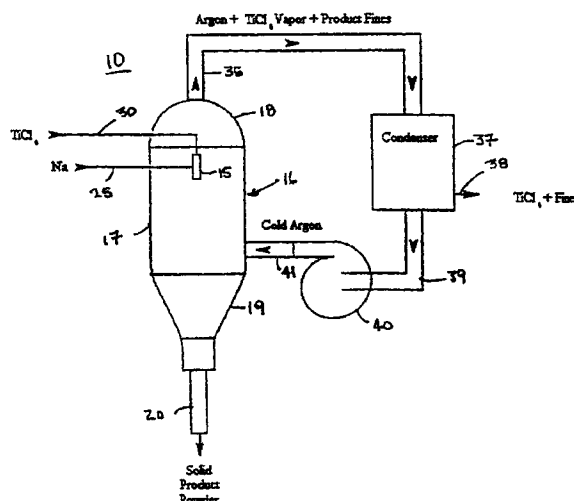
(75) Inventors/Applicants (*for US only*): **ANDERSON,
Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills,
IL 60514 (US). **ARMSTRONG, Donn** [US/US]; 6005
Ridge Court, Lisle, IL 60532 (US). **JACOBSEN, Lance**
[US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

[Continued on next page]

(54) Title: SYSTEM AND METHOD OF PRODUCING METALS AND ALLOYS



(57) Abstract: A system for producing an elemental material or an alloy thereof from a halide of the elemental material or halide mixtures comprising a reactor for introducing the vapor halide of an elemental material or halide mixtures thereof into a liquid phase of a reducing metal of an alkali metal or alkaline earth metal or mixtures thereof present in less than or equal to the amount needed to reduce the halide vapor to the elemental material or alloy resulting in an exothermic reaction between the vapor halide and the liquid reducing metal producing particulate elemental material or alloy thereof and particulate halide salt of the reducing metal, a chamber wherein the reaction products are cooled so that substantially all the particulate elemental material or alloy remains unsintered, and a separator for separating the particulate metal or alloy reaction products from the particulate salt.

WO 2004/033737 A1



For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SYSTEM AND METHOD OF PRODUCING METAL AND ALLOYS

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on U.S. Provisional Application Serial No. 60/416,611 October 7, 2002 and U.S. Provisional Application Serial No. 60/327,865 filed October 9, 2001.

BACKGROUND OF THE INVENTION

This invention relates to the production and separation of elemental material from the halides thereof and has particular applicability to those metals and non metals for which a reduction of the halide to the element is exothermic. Particular interest exists for titanium, and the present invention will be described with particular reference to titanium, but is applicable to other metals and non metals such as aluminum, arsenic, antimony, beryllium, boron, tantalum, gallium, vanadium, niobium, molybdenum, iridium, rhenium, silicon osmium, uranium, and zirconium, all of which produce significant heat upon reduction from the halide to the metal. For the purposes of this application, elemental materials include those metals and non metals listed above or in Table 1 and the alloys thereof.

This invention relates to the separation methods disclosed in U.S. patent no. 5,779,761, U.S. patent no. 5,958,106 and U.S. patent no. 6,409,797, the disclosures of which are incorporated herein by reference. The above-mentioned '761, '106 and '797 patents disclose a revolutionary method for making titanium which is satisfactory for its intended purposes and in fact continuously produces high grade titanium and titanium alloys by introducing halide vapor(s) of the element or alloy to be produced into the liquid phase of a reducing metal, instantaneously to initiate an exothermic reaction and to control the temperature of the reaction products by providing excess amounts of reducing metal to absorb the heat of reaction. The present invention resides the discovery that by introducing the halide vapor(s) of the element or alloy to be produced into the liquid phase of a reducing metal where the reducing metal is present in an amount equal to or less than the stoichiometric amount required to produce the elemental material (or alloy) coupled with extraneous cooling, if necessary, of the reaction products, continuous production of the elemental material (or alloy) can still be obtained,

while preventing the produced material from sintering.

Previously, the Armstrong process used excess reducing metal to absorb heat produced during the exothermic reaction resulting in a startling new process. It is now believed that using an excess of halide vapor to absorb some of the heat of reaction alone or in combination with extraneous cooling produces many of the benefits heretofore obtained with the process of the '761, '106 and '797 patents. It is also believed that use of stoichiometric quantities of reducing metal and halide vapor in combination with extraneous cooling will produce many of the benefits heretofore obtained with the process of the '761, '106 and '797 patents.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method and system for producing metals or non metals or alloys thereof by an exothermic reaction between vapor phase halides and a liquid reducing metal in which excess amounts of the vapor phase halides are present to absorb some of the heat of reaction and the products produced thereby.

Yet another object of the present invention is to provide an improved method and system for producing elemental materials or an alloy thereof by an exothermic reaction of a vapor halide of the elemental material or materials or halide mixtures thereof in a liquid reducing metal in which excess vapor halide in combination with a sweep gas is used to cool the products of the exothermic reaction and the products produced thereby.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of a system for practicing one method of the present invention;

FIG. 2 is a schematic representation of another system for practicing another embodiment of the present invention; and

FIG. 3 is a schematic representation of another system of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to Figure 1 of the drawings, there is disclosed a system 10 for the practice of the invention. The system 10 includes a reactor 15 generally vertically displaced in this example in a drop tower vessel 16, the drop tower 16 having a central generally cylindrical portion 17, a dome top 18 and a frustoconical shaped bottom portion 19. A product outlet 20 is in communication with the frustoconical portion 19. The reactor 15 essentially consists of an apparatus illustrated in Figure 2 of U.S. patent no. 5,958,106 in which a tube through which liquid metal flows as a stream has inserted therein a halide(s) vapor so that the vapor halide(s) is introduced into the liquid reducing metal below the surface, preferably through a choke flow nozzle and is entirely surrounded by the liquid metal during the ensuing exothermic reaction; however, it may be that because the amount of halide is either the stoichiometric amount necessary to react with all the reducing metal or in excess of that amount, some surface reactions may occur. In such case, additional process steps may be required.

A reducing metal inlet pipe 25 enters the reactor 15 near the top 18 and a vapor halide inlet 30 also enters the drop tower 16 near then top 18. However, it will be understood by a person of ordinary skill in the art that a variety of configurations of inlet conduits may be used without departing from the spirit and scope of the present invention.

As illustrated, there is an overhead exit line 35 through which vapor leaving reactor 15 can be drawn. The overhead exit line 35 leads to a condenser 37 where certain vapors are condensed and discharged through an outlet 38 and other vapor or gas, such as an inert gas, is pumped by a pump 40 through a heat exchanger (not shown) and line 41 into the drop tower 16, as will be explained.

For purposes of illustration, in Figure 1 there is shown a reducing metal of

sodium. It should be understood that sodium is only an example of reducing metals which may be used in the present invention. The present invention may be practiced with an alkali metal or mixtures of alkali metals or an alkaline earth metal or mixtures of alkaline earth metals or mixtures of alkali and alkaline earth metals. The preferred alkali metal is sodium because of its availability and cost. The preferred alkaline earth metal is magnesium for the same reason.

The preferred halide(s) to be used in the process of the present invention is a chloride, again because of availability and cost. The metals and non-metals which may be produced using the subject invention are set forth in Table 1 hereafter; the alloys of the metals and non-metals of Table 1 are made by introducing mixed halide vapor into the reducing metal.

TABLE 1

FEEDSTOCK	HEAT kJ/g
TiCl ₄	-5
AlCl ₃	-5
SbCl ₃	-4
BeCl ₂	-6
BCl ₃	-8
TaCl ₅	-4
VCl ₄	-6
NbCl ₅	-5
MoF ₅	-10
GaCl ₃	-5
UF ₆	-4
ReF ₆	-8
ZrCl ₄	-4
SiCl ₄	-11

All of the feedstocks (in various combinations) as chlorides or other halides in Table 1 result in an exothermic reaction with an alkali metal or alkaline earth metal to provide the halide(s) of the reducing metal and the metal or alloy of the halides introduced into the reducing metal. Ti is discussed only by way of example and is not meant to limit the invention. Because of the large heat of reaction, there has been the problem that the reaction products fuse into a mass of material which is difficult to process, separate and purify. Discussions of the Kroll and Hunter processes appear in the patents referenced above.

The patents disclosing the Armstrong process show methods and systems of producing a variety of metals and alloys and non-metals in which the heat of reaction resulting from the exothermic reaction is controlled by the use of excess

liquid reducing metal. The reaction proceeds instantaneously by introducing the metal halide into a continuous phase of liquid reducing metal, otherwise described as a liquid continuum, at the temperatures illustrated. The use of a subsurface reaction described in the Armstrong process has been an important differentiation between the batch processes and other suggested processes for making metals such as titanium and the processes disclosed in the Armstrong et al. patents.

Nevertheless, the use of excess liquid reducing metal requires that the excess liquid metal be separated before the products can be separated. This is because the excess liquid reducing metal may explosively react with water or is insoluble in water whereas the particulate products of the produced metal and the produced salt can be separated with water wash.

By way of example, when titanium tetrachloride in vapor form is injected into sodium liquid, an instantaneous reaction occurs in which titanium particles and sodium chloride particles are produced along with the heat of reaction. Excess sodium absorbs sufficient heat that the titanium particles do not sinter to form a solid mass of material. Rather, after the excess sodium is removed, such as by vacuum distillation suggested in the aforementioned Armstrong patents, the remaining particulate mixture of titanium and sodium chloride can be easily separated with water.

Nevertheless, vacuum distillation is expensive and it is preferred to find systems and methods that will permit the separation of the particulate reaction products of the reaction directly with water without the need of preliminary steps. This has been accomplished in the present invention by the discovery that using stoichiometric amounts of reactants or excess halide vapor to absorb some of the heat of reaction, with or without extraneous cooling, significant advantages of the Armstrong process may be retained. For instance, using an excess halide vapor as a heat sink results in particulate products and only vapor phase halide which can be efficiently and inexpensively removed so that the particulates accumulating at the bottom 19 of the reaction vessel or drop tower 16 are entirely free of liquid reducing metal, thereby permitting the separation of the particulate reaction products with water, obviating the need for a separate vacuum distillation step.

In the reactor 15, as previously taught in the Armstrong patents, the

continuous liquid phase of sodium (or other reducing metal) is established into which the titanium tetrachloride vapor is introduced and instantaneously causes an exothermic reaction to occur producing large quantities of heat, and particulates of titanium metal and sodium chloride. The boiling point of sodium chloride is 1465°C and becomes the upper limit of the temperature of the reaction products, whereas the boiling point of titanium tetrachloride is the lower limit of the temperature of the reaction products to ensure that all excess titanium tetrachloride remains in the vapor phase until separation from the particulate reaction products. A choke flow nozzle also known as a critical flow nozzle is well known and is used in the line transmitting halide vapor into the liquid reducing metal, all as previously disclosed in the '761 and '106 patents. It is critical for the present invention that stoichiometric quantities of reactants with extraneous cooling or that excess halide vapor such as TiCl_4 be available with or without extraneous coolants to absorb the heat of reaction to control the temperature of the reaction products.

The vapors exiting the reactor 15 are drawn through exit line 35 along with an inert sweep gas introduced through the inert gas inlet 41. The inert gas, in this example argon, may be introduced at a temperature of about 200°C, substantially lower than the temperature of the reaction products which exit the tower 16. The argon sweep gas flows, in the example illustrated in Fig. 1, countercurrently to the direction of flow of the particulate reaction products. The excess titanium tetrachloride vapor is swept by the argon into the outlet 35 along with whatever product fines are entrained in the gas stream comprised of argon and titanium tetrachloride vapor at an elevated temperature and transmitted to the condenser 37. In the condenser 37, heat exchange occurs in which the titanium tetrachloride vapor is cooled to about 200°C and recycled to the titanium tetrachloride feed or inlet 30 via line 38 and the argon is also cooled to about 200°C temperature at which it is recycled. It is seen therefore, that the inert gas preferably flows in a closed loop and continuously recirculates as long as the process is operational. The product fines present in the condenser 37 will

be removed by filters (not shown) in both the titanium tetrachloride recycling line 38 and in the line 39 exiting the condenser 37 with the inert gas.

As the inert gas moves upwardly through the vessel or drop tower 16, there is contact between the colder inert gas and the reaction particulates which are at a higher temperature. Excess titanium tetrachloride vapor exits the drop tower 16 at an elevated temperature while the particulate product exits the reactor 15 at a temperature not greater than 1465°C. After being cooled by contact with the argon gas, the particulate product, in this example, leaves the vessel 16 and enters a cooler (not shown), to exit therefrom at about 50°C. Thereafter, the product may be introduced to a water wash to separate the metal particulates. The titanium particulates exit from the water wash for drying and further processing.

It should be understood that although titanium is shown to be the product in Fig. 1 any of the elements or alloys thereof listed in Table 1 may be produced by the method of the present invention. The most commercially important metals at the present time are titanium and zirconium and their alloys. The most preferred titanium alloy for defense use is 6% aluminum, 4% vanadium, the balance substantially titanium. This alloy known as 6:4 titanium is used in aircraft industry, aerospace and defense. Zirconium and its alloys are important metals in nuclear reactor technology. Other uses are in chemical processing equipment.

The preferred reducing metals because of cost and availability are sodium of the alkali metals and magnesium of the alkaline earth metals. The boiling point of magnesium chloride is 1418°C. Therefore, if magnesium were to be used rather than sodium as the reducing metal, then preferably the product temperature would be maintained below the boiling point of magnesium chloride. The chlorides are preferred because of cost and availability.

One of the significant features of the present invention is the complete separation of the particulate reaction products from any left over reactants as the reaction products leave the reactor 15 thereby providing at the bottom of the drop tower 16 a product which may then be separated with water in an inexpensive and uncomplicated process. If liquid sodium or other reducing metal is trapped within the product particulates, it must be removed prior to washing. Accordingly, the invention as described is an advance with respect to the separation of the metal or

alloy particulates after production as disclosed in the aforementioned Armstrong et al. patents and application.

Referring to Figure 2, there is disclosed another embodiment of the present invention system 110 which includes a reactor 115 disposed within a drop tower 116 having a cylindrical center portion 117, a dome topped portion 118 and a frustoconical bottom portion 119 connected to a product outlet 120. A plurality of cooling coils 121 are positioned around the frustoconical portion 119 of the drop tower 116 for a purpose to be explained.

As in the system 10 shown in Fig. 1, there is a metal halide inlet 130 and a reducing metal inlet 125 in communication with the reactor 115 disposed within the drop tower 116. An overhead exit line 135 leads from the dome top portion 118 of the drop tower 116 to a condenser 137 in fluid communication with a pump 140. An excess vapor and product fine outlet 138 is also provided from the condenser 137.

In operation, the system 110 is similar to the system 10 in that a liquid reducing metal, for instance sodium or magnesium, is introduced via inlet 125 from a supply thereof at a temperature above the melting point of the metal, (the melting point of sodium is 97.8°C and for Mg is 650°C) such as 200°C for sodium and 700°C for Mg. The vapor halide of the metal or alloy to be produced, in this example titanium tetrachloride, is introduced from the boiler at a temperature of about 200°C to be injected as previously discussed into a liquid so that the entire reaction occurs instantaneously and is at least initially subsurface. The products coming from the reactor 115 include particulate metal or alloy, and particulate salt of the reducing metal. Also, excess vapor halide of the metal or alloy to be produced may be present. In the system 110, there is no sweep gas but the drop tower 116 is operated at a pressure slightly in excess of 1 atmosphere and this in combination with the vacuum pump 140 causes any excess vapor halide leaving the reactor 115 to be removed from the drop tower 116 via the line 135. A certain amount of product fines may also be swept away with the halide vapor during transportation from the drop tower 116 through the condenser 137 and the excess titanium tetrachloride vapor outlet 138. A filter (not shown) can be used to separate any fines from the vapor in line 138.

Cooling coils 121 are provided, as illustrated on the bottom 119 of the drop tower 116. A variety of methods may be used to cool the drop tower 116 to reduce the temperature of the product leaving the drop tower 116 through the product outlet 120. As illustrated in Fig. 2, a plurality of cooling coils 121 may be used or alternatively, a variety of other means such as heat exchange fluids in contact with the container or heat exchange medium within the drop tower 116. What is important is that the product be cooled while the excess TiCl_4 remains a vapor so that the vapor phase can be entirely separated from the product prior to the time that the product exits the drop tower 116 through the product outlet 120.

Referring now to Figure 3, there is disclosed another embodiment of the invention. A system 210 in which like parts are numbered in the 200 series as opposed to the 100 series. Operation of the system 210 is similar to the operation of the system 10 but in the system 210 an inert sweep gas flows co-currently with the product as opposed to the countercurrent flow as illustrated in system 10 and Figure 1. In the system 210 illustrated in Fig. 3, the gas flow is reversed in comparison to the system 10. In the system 210, the sweep gas such as argon, the excess (if any) titanium tetrachloride vapor, and the product of titanium particles and sodium chloride exit through the outlet 220 into a demister or filter 250. The demister or filter 250 is in fluid communication with a condenser 237 and a pump 240 so that the excess titanium tetrachloride (if any) vapor and the argon along with whatever fines come through the demister or filter 250 are transported via a conduit 252 to the condenser 237. In the condenser 237, the excess titanium tetrachloride vapor is cooled, the fines are separated while the argon or inert gas is cooled and recycled via the pump 240 in line 235 to the drop tower 216. The inert gas may have to be separated from excess titanium tetrachloride, which can be accomplished by appropriate condensing of the TiCl_4 . The other apparatus of the system 210 bear numbers in the 200 series that correspond to the numbers in the system 10 and 100 and represent the same part functioning in the same or similar manner.

It is seen that the present invention can be practiced with a sweep gas that is either countercurrent or co-current with the reaction products of the exothermic reaction between the halide and the reducing metal or without a sweep gas. An

important aspect of the invention is the separation of any excess halide vapor prior to the separation of the produced metal and the produced salt. Because excess halide vapor is used as a heat sink or a cooling gas to control the temperatures of the reaction products due to the large heat of reaction, it is possible that conditions may be present which do not occur with the processes taught in the Armstrong et al. '761 or '106 patents. For instance, when titanium tetrachloride is present in excess of the stoichiometric amount needed to react with the reducing metal, certain subchlorides, such as TiCl_3 or TiCl_2 , may be formed. Subchlorides are to be avoided, since they may contaminate the produced titanium, requiring further processing. Moreover, it is possible that some of the reaction between the reducing metal, for instance sodium, and the halide, for instance titanium tetrachloride, may not be subsurface. This is not preferred because the thermodynamics of a surface reaction are different than a subsurface reaction.

Various alloys can be made using the process of the present invention. For instance, titanium alloys including aluminum and vanadium can be made by introducing predetermined amounts of aluminum chloride and vanadium chloride and titanium chloride to a boiler or manifold and the mixed halides introduced into liquid reducing metal. For instance, grade 5 titanium alloy is 6% aluminum and 4% vanadium. Grade 6 titanium alloy is 5% aluminum and 2.5% tin. Grade 7 titanium is unalloyed titanium and paladium. Grade 9 titanium is titanium alloy containing 3% aluminum and 2.5% vanadium. Other titanium alloys include molybdenum and nickel and all these alloys may be made by the present invention.

Accordingly, there has been disclosed an improved process for making and separating the products of the Armstrong process resulting from the exothermic reaction of a metal halide with a reducing metal. A wide variety of important metals and alloys can be made by the Armstrong process and separated according to this invention.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of producing an elemental material or an alloy thereof from a halide of the elemental material or halide mixtures comprising introducing the vapor halide of an elemental material or halide mixtures thereof into a liquid phase of a reducing metal of an alkali metal or alkaline earth metal or mixtures thereof present in less than or equal to the amount needed to reduce the halide vapor to the elemental material or alloy resulting in an exothermic reaction between the vapor halide and the liquid reducing metal producing particulate elemental material or alloy thereof and particulate halide salt of the reducing metal, cooling the reaction products so that substantially all the particulate elemental material or alloy remains unsintered, and separating the particulate reaction products.
2. The method of claim 1, wherein the elemental material or alloy is one or more of Ti, Al, Sb, Be, B, Ga, Mo, Nb, Ta, V, Zr, U, Re, Si, Os, Ir and mixtures thereof.
3. The method of claim 2, wherein the reducing metal is an alkali metal.
4. The method of claim 3, wherein the reducing metal is Na.
5. The method of claim 4, wherein the elemental material or an alloy thereof includes titanium and the Na is flowing.
6. The method of claim 2, wherein the reducing metal is an alkaline earth metal.
7. The method of claim 6, wherein the reducing metal is Mg.
8. The method of claim 7, wherein the elemental material or alloy thereof includes titanium and the Mg is flowing.
9. The method of claim 2, wherein the alloy is substantially Ti and Al and V and is formed by introducing the chlorides thereof as vapor into a liquid phase of a reducing metal.
10. The method of claim 2, wherein the particulate reaction products are cooled with an inert sweep gas.
11. The method of claim 9, wherein the reducing metal is Na, the inert sweep gas is Ar and the alloy is Ti - 6% by weight Al- 4% by weight V.

12. The method of claim 9, wherein the reducing metal is Mg, the inert sweep gas is Ar and the alloy is Ti-6% by weight Al - 4% by weight V.

13. The method of claim 1, wherein the temperature of the particulate elemental material or alloy thereof is maintained at or below the boiling point of the halide salt of the reducing metal.

14. The method of claim 10, wherein the inert sweep gas flows countercurrently to the particulate reaction products.

15. The method of claim 10, wherein the inert sweep gas flows concurrently with the particulate reaction products; and further including filtering the particulate reaction products from the sweep gas.

16. The method of claim 1, wherein the particulate reaction products move in one direction and are cooled by contact with an inert gas flowing countercurrently to the particulate reaction products, the inert gas separating any excess vapor halide of the elemental material or halide mixtures thereof present from the particulate reaction products before separation of the particulate halide salt of the reducing metal from elemental material or alloy thereof.

17. The method of claim 16, wherein the cooled particulate reaction products are contacted with water to separate the halide salt of the reducing metal from particulate elemental material or alloy thereof.

18. A method of producing a metal element or an alloy thereof in an exothermic reaction between the chloride of the metal element or the chlorides of the constituents of the alloy and a reducing metal of an alkali metal or an alkali earth metal or mixtures thereof, comprising establishing a liquid phase of the reducing metal and introducing the vapor chloride or vapor chlorides of the metal or alloy to be produced into the liquid phase of the reducing metal in an amount equal to or less than the stoichiometric amount needed to react with the reducing metal to produce particulate reaction products of the metal element or alloy thereof and particulate chloride salt of the reducing metal and heat, cooling the reaction products to prevent sintering of the particulate metal element or alloy, and separating the cooled particulate metal element or alloy from the chloride salt of the reducing metal.

19. The method of claim 18, wherein the particulate reaction products are

cooled by contact with flowing gas cooler than the reaction products.

20. The method of claim 19, wherein the flowing gas is inert with respect to the particulate reaction products and flows through the particulate products to cool the particulate reaction products and to separate any chloride vapor from the particulate reaction products.

21. The method of claim 20, wherein the metal element is Ti or alloys thereof or Zr or alloys thereof and the reducing metal is Na or an alkaline earth metal.

22. The method of claim 21, wherein the alkaline earth metal is Mg.

23. The method of claim 21, wherein the metal element is Ti.

24. The method of claim 21, wherein the alloy includes Ti and V and Al.

25. The method of claim 18, wherein any excess halide vapor present is separated from the reaction products.

26. A product made by the method of claim 1.

27. A product made by the method of claim 18.

FIG 1

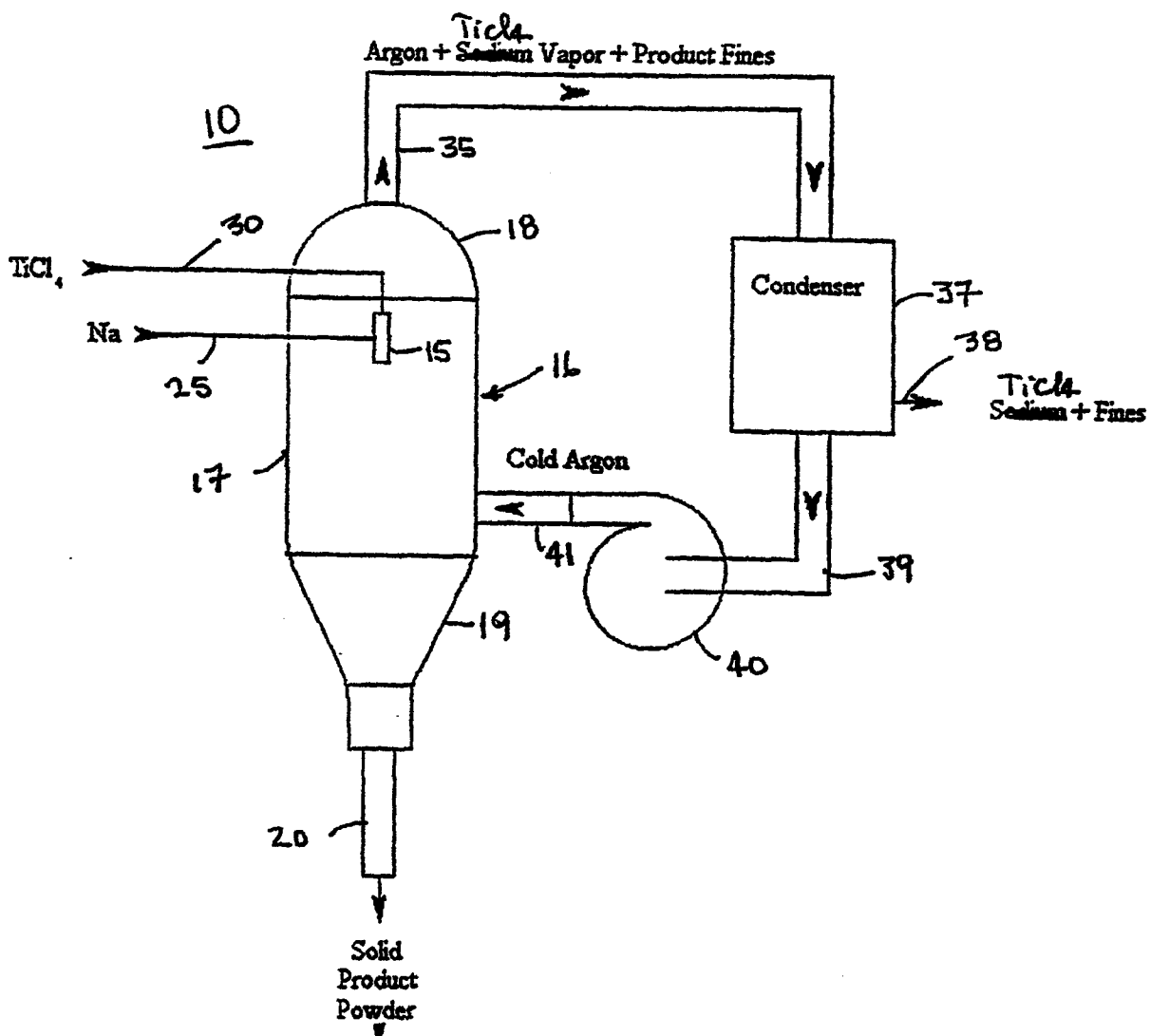
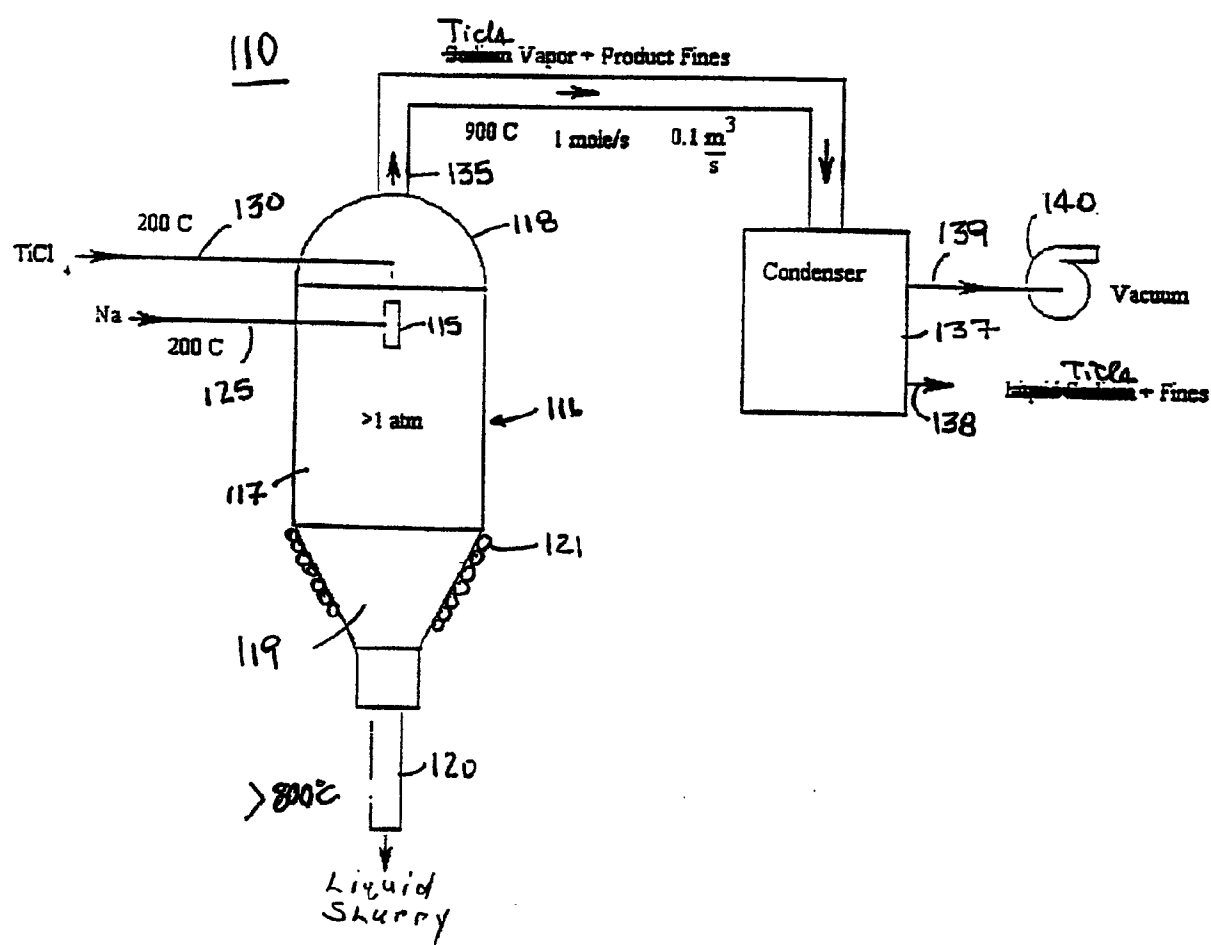
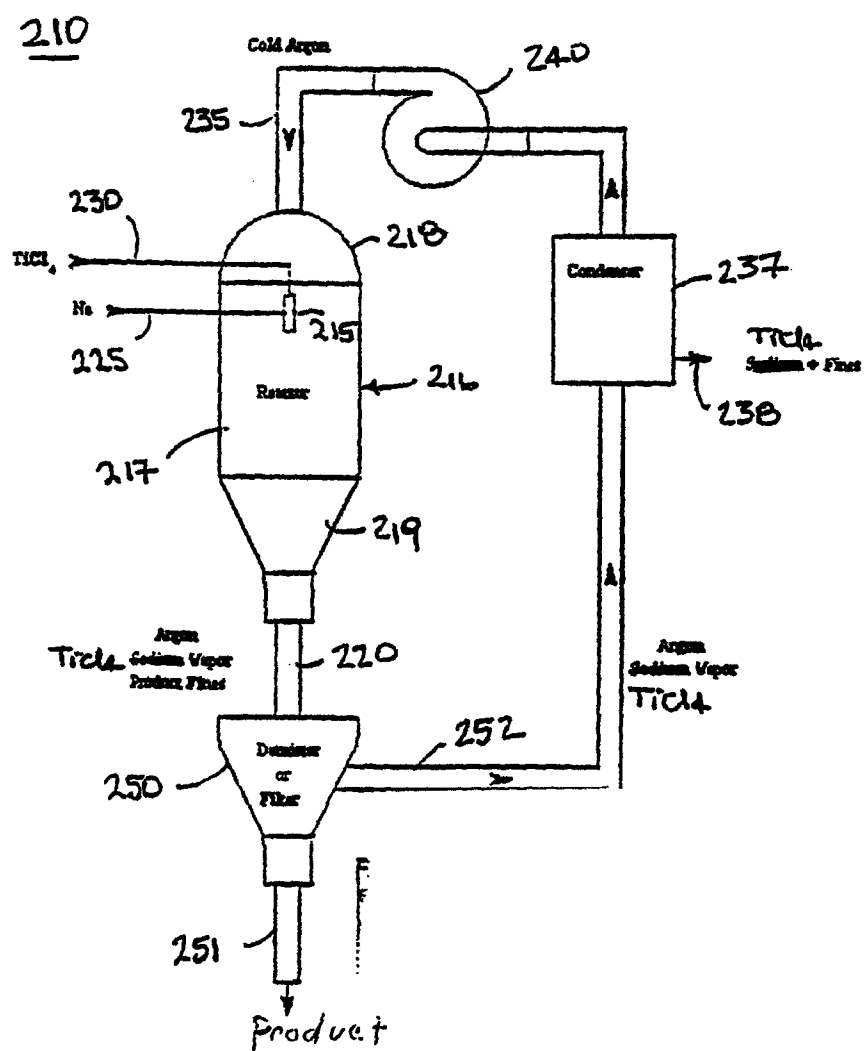


Fig. 2





INTERNATIONAL SEARCH REPORT

International No
PCT/US 03/27659

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C22B34/12 B22F9/28 C22C1/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C22B B22F C22C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 827 371 A (PATERSON QUIN JAMES) 18 March 1958 (1958-03-18) column 1, line 41 - column 2, line 2; figure 2; example 2 column 5, line 28 - line 34	1-15, 17-27
A	US 2002/0005090 A1 (ANDERSON RICHARD PAUL ET AL) 17 January 2002 (2002-01-17)	1
X	claims	18, 26, 27
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search 28 January 2004		Date of mailing of the international search report 12.02.04
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Alvazzi Delfrate, M

INTERNATIONAL SEARCH REPORT

Internat application No.
PCT/US 03/27659

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-17, 26

A method wherein the liquid phase of the reducing metal is present in an amount less than or equal to the amount needed to reduce the halide vapour to the elemental material or alloy and the product of said method.

2. claims: 18-25, 27

A method wherein the liquid phase of the reducing metal is present in an amount in excess than or equal to the amount needed to reduce the halide vapour to the elemental material or alloy, the halide is chloride and the product of said method.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 03/27659

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2827371	A	18-03-1958	GB 717930 A
			03-11-1954
			BE 515246 A
			15-08-1955
			CH 308890 A
			15-03-1958
			CH 328601 A
			10-04-1958
			DE 1027881 B
US 2002005090	A1	17-01-2002	FR 1069706 A
			12-07-1954
			LU 31781 A1
			NL 77870 C
			NL 173516 B
			US 5958106 A
			28-09-1999
			US 5779761 A
			14-07-1998
US 2002005090	A1	17-01-2002	US 2002148327 A1
			17-10-2002
			US 2002152844 A1
			24-10-2002
			US 2003145682 A1
			07-08-2003
			US 2003061907 A1
			03-04-2003
			AU 686444 B2
			05-02-1998
			AU 3320195 A
			04-03-1996
			BR 9508497 A
			23-12-1997
			CA 2196534 A1
			15-02-1996
			CN 1161064 A , B
			01-10-1997
			DE 69521432 D1
			26-07-2001
			DE 69521432 T2
			29-05-2002
			EP 0777753 A1
			11-06-1997
			ES 2161297 T3
			01-12-2001
			JP 10502418 T
			03-03-1998
			JP 3391461 B2
			31-03-2003
			KR 241134 B1
			02-03-2000
			NO 970444 A
			26-03-1997
			RU 2152449 C1
			10-07-2000
			WO 9604407 A1
			15-02-1996

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
10 June 2004 (10.06.2004)

PCT

(10) International Publication Number
WO 2004/048622 A1

(51) International Patent Classification⁷: **C22B 9/02**,
9/04, 34/12

Richard [US/US]; 5836 Sunrise Avenue, Clarendon Hills,
IL 60514 (US). JACOBSEN, Lance [US/US]; 123 San
Carlos Road, Minooka, IL 60447 (US).

(21) International Application Number:
PCT/US2003/027649

(74) Agent: LEVY, Harry, M.; Emrich & Dithmar, 300 South
Wacker Drive, Suite 3000, Chicago, IL 60606 (US).

(22) International Filing Date:
3 September 2003 (03.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/427,728 20 November 2002 (20.11.2002) US

(71) Applicant (for all designated States except US): INTER-
NATIONAL TITANIUM POWDER, LLC. [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

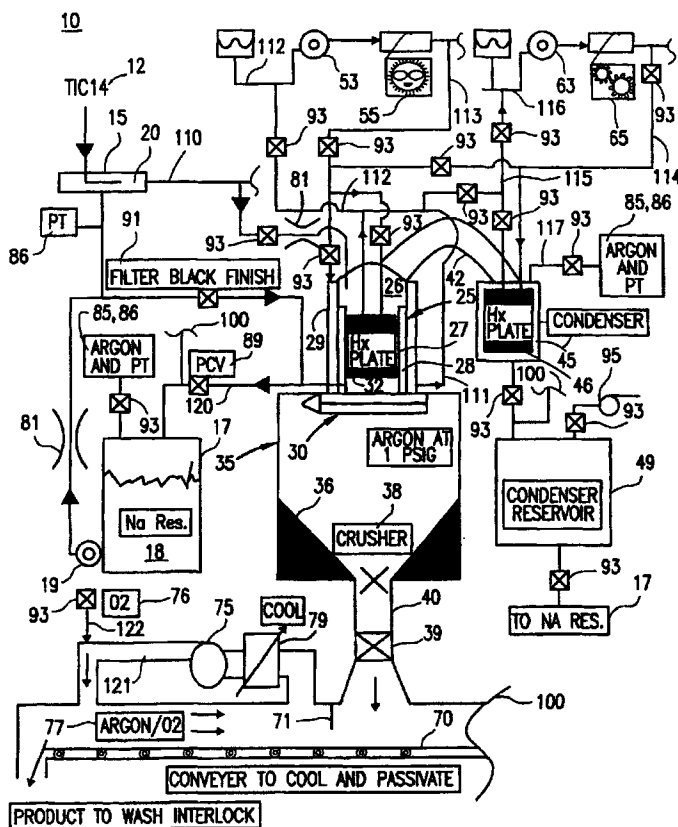
(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,

(72) Inventors; and
(75) Inventors/Applicants (for US only): ANDERSON,

[Continued on next page]

(54) Title: SEPARATION SYSTEM OF METAL POWDER FROM SLURRY AND PROCESS



(57) Abstract: A system and method of separating metal powder from a slurry of liquid metal and metal powder and salt is disclosed in which the slurry is introduced into a first vessel operated in an inert environment when liquid metal is separated from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal. The salt and metal powder is transferred to a second vessel operated in an inert environment with both environments being protected from contamination. Then the salt and metal powder are treated to produce passivated powder substantially free of salt and liquid metal. The method is particularly applicable for use in the production of Ti and its alloys.



ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— *with international search report*

SEPARATION SYSTEM OF METAL POWDER FROM SLURRY AND PROCESS.

Background of the Invention

This invention relates to a separation system and process as illustrated in Fig. 1 useful for the product produced by Armstrong method as disclosed and claimed in U.S. Patents 5,779,761; 5,958,106 and 6,409,797, the disclosures of each and every one of the above-captioned patents are incorporated by reference.

Summary of the Invention

A principal object of the invention is to provide a separation system for the Armstrong process disclosed in the '761, '106 and '797 patents;

Another object of the invention is to provide a continuous separation system.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

Brief Description of the Drawings

Figure 1 is a schematic illustration of the separation system of the present invention.

Detailed Description of the Invention

The system 10 of the present invention deals with the separation of a metal, alloy or ceramic product, such as titanium, for example only, from the reaction products in the Armstrong process. Although the Armstrong process is applicable to a wide variety of exothermic reactions, it is principally applicable to metals, mixtures, alloys and ceramics disclosed in the above-mentioned patents. The product of Armstrong process is a slurry of excess reductant metal, product metal and alloy or ceramic and salt produced from the reaction. This slurry has to be separated so that various parts of it can be recycled and the produced metal, alloy or ceramic separated and passivated if necessary.

Turning now to the schematic illustration of the system and process of the present invention illustrated in Fig. 1, there is disclosed in the system 10 a source of, for illustration purposes only, titanium tetrachloride 12 which is introduced into a reactor

15 of the type hereinbefore disclosed in the Armstrong process. A supply tank or reservoir 17 with a supply of sodium (or other reductant) 18 is transferred by a pump 19 to the reactor 15 wherein a slurry product 20 of excess reductant and metal, alloy or ceramic, and salt is produced at an elevated temperature, all as previously described in the incorporated patents.

The slurry product 20 is transferred to a vessel 25 which is in the illustration dome-shaped, but not necessarily of that configuration, the vessel 25 having an interior 26 into which the slurry product 20 is introduced. A filter 27, preferably but not necessarily cylindrical, is positioned within the interior 26 and defines an annulus 28, the slurry product 20 being received inside the cylindrical filter 27. An annular heat exchanger 29 is positioned around the vessel 25, all for a purpose hereinafter disclosed.

The vessel 25 further includes a moveable bottom closure 30. Heat exchange plates 32 are connected as will hereinafter be described to an isolated heating system 50. A collection vessel 35 is positioned below the vessel 25 and is sealed therefrom by the moveable bottom closure 30. The collection vessel 35 has an inwardly sloping bottom surface 36 which leads to a crusher 38 and a valve 39 in the outlet 40 of the collection vessel 35.

Finally, a vapor conduit 42 interconnects the top of the vessel 25 and particularly the interior 26 thereof with a condenser vessel 45, the condenser vessel having a heat exchange plate 46 connected, as hereinafter described, to an isolated cooling system 60. The condenser 45 is connected to a condenser reservoir 49, the condensate collected therein being routed to the sodium supply tank or reservoir 17.

The isolated heating system 50 includes a head tank 52 for the heating fluid which is moved by pump 53 to the heater 55 as will be hereinafter described, connected to both the heat exchanger 29 surrounding the vessel 25 and the heat exchange plates 32 interior of the vessel 25. The isolating cooling system 60 also is provided with a head tank 62, a pump 63 and a cooler 65 which serves to cool the cooling fluid circulated in an isolated loop to the cooling plates 46 as will be hereinafter set forth.

Below the valve 39 and the collection vessel 35 is a product conveyor 70 having a baffle or cake spreader 71 extending downwardly toward the conveyor 70. The

conveyor 70 onto which the produced metal, alloy or ceramic and salt are introduced from the collection vessel 35, after removal of the excess reductant metal, is contacted with a counter current flow of gas, preferably but not necessarily oxygen and argon, 77 from a blower 75 in communication with a supply 76 of oxygen and the supply of inert gas such as argon. The heat exchanger 79 is in communication with the blower 75 so as to cool the oxygen/argon mixture 77 as it flows in counter current relationship with the produced metal, alloy or ceramic on the conveyor 70, thereby to contact the product particulates with oxygen to inert the produced metal, alloy or ceramic when required but not so much as to contaminate the produced material.

As indicated in the flow sheet of Fig. 1, there are a plurality of flow meters 81 distributed throughout the system, as required and as well known in the engineering art. There are pressure transducers 86 and pressure control valves 89 where required, all within the engineering skill of the art. A back filter valve 91 is provided in order to flush the filter 27 if necessary. Additionally, a variety of standard shut-off valves 93 are positioned within the loop, hereinafter to be explained and as required. A vacuum pump 95 is used to draw a vacuum in the vessel 25, as will be explained, and the symbol indicated by reference numeral 100 indicates that a plurality of the same or similar systems may be operating at any one time, it being remembered that the enclosed figure is for a single reactor 15 and one separation vessel 25, wherein as in a commercial production plant, a plurality of reactors 15 may be operating simultaneously each reactor 15 may have more than one separation vessel 25, all depending on engineering economics and ordinary scale up issues.

Product 20 from the reactor 15 exits through line 110 and enters vessel 25 at the top thereof. Although line 110 is shown entering above the filter 27, preferably the line 110 and filter 27 are positioned so that slurry 20 is introduced below the top of filter 27 or in the center of the filter or both. As described in the previously incorporated patents, the slurry product 20 consists of excess reductant metal, salt formed by the reaction and the product of the reaction which in this specific example is titanium existing as solid particles. The product 20 in slurry form from the reactor 15 is at an elevated temperature depending on the amount of excess reductant metal present, the heat capacity thereof and other factors in the reactor 15 during operation of the Armstrong

process. In the vessel 25 is a filter 27 which occupies a portion of the interior 26 of the vessel 25, the interior optionally being heated with the annular heat exchanger 29. The slurry product 20 is directed to the interior of the filter 27 where the slurry contacts the heat exchange plates 32.

In the heating system 50, the heat exchange fluid in the plates 32 pass with the heat exchange fluid from the annular heat exchanger 29 through line 111 to the line 112 which connects the heat exchange medium supply in the head tank 52 to the heat exchanger 55. Fluid moves from the heater 55 through the heat exchange plates 32 by means of the pump 53 as the heated heat exchange fluid flows out of the heat exchanger 55 through line 113 and back into the heat exchange plates 32 and/or the annular heat exchanger 29. Because the heating system 50 is a closed loop, the heat exchange fluid may or may not be the same as the reductant metal used in the reactor 15. NaK is shown as an example because of the low melting point thereof, but any other suitable heat exchange fluid may be used. Suitable valves 93 control the flow of heat exchange fluid from the heater 55 to either or both of the heat exchanger 29 and plates 32. Preferably, the plates 32 are relatively close together, on the order of a few inches, to provide more heat to the cake which forms as excess reductant metal vaporizes. Moreover, closer plates 32 reduce the path length the heat has to travel and the path length the excess reductant metal vapor travels through the forming cake, thereby to reduce the time required to distill and remove excess reductant metal from the vessel 25. Exact spacing of the plates 32 depends on a number of factors, including but not limited to, the total surface area of the plates, the heat transfer coefficient of the plates, the amount of reductant metal to be vaporized and the temperature differential between the inside and the outside of the plates.

When the slurry product 20 comes out of the reactor 15, it is at a pressure at which the reactor 15 is operated, usually up to about two atmospheres. The product slurry 20 enters the inside of filter 27 under elevated pressure and gravity results in the liquid reductant metal being expressed through the filter 27 into the annular space 28 and fed by the line 120 into the reservoir 17. The driving force for this portion of the separation is gravity and the pressure differential between the reactor 15 and the inlet pressure of pump 19. If required the annulus 28 may be operated under vacuum to

assist removal of liquid reductant metal, or the pressure in vessel 25 may be increased during the deliquoring of the reductant metal. After sufficient liquid metal has drained through the filter 27 by the aforementioned process, the PCV valve 89 is closed and other valves 93 are closed to isolate vessel 25 and then the valve 93 to the vacuum pump 95 is opened, whereupon a vacuum is established in the interior 26 of vessel 25. Heating fluid (liquid or vapor, for instance Na vapor) is directed into the heat exchanger plates 32 to boil the remaining reductant metal 18 producing a filter cake. The temperature in vessel 25 is elevated sufficiently to vaporize remaining liquid metal reductant 18 therein which is drawn off through conduit 42 to the condenser 45. The conduit 42 is required to be relatively large in diameter to permit rapid evacuation of the interior 26 of the vessel 25. Because the pressure drop between the vessel 25 and the condenser 45, during vaporization of the reductant metal 18 is low, the specific volume is high and the mass transfer low, requiring a large diameter conduit 42. Boiling the reductant metal on the shell side is accomplished by heat exchange with a heated fluid on the tube side.

The annular heat exchanger 29 is optionally operated to maintain the expressed liquid in the annulus 28 at a sufficient temperature to flow easily and/or to provide additional heat to the vessel 25 to assist in vaporization of excess reductant metal from the interior 26 thereof. After liquid metal reductant vapor has been removed from the interior 26 of the vessel 25, a filter cake remains from the slurry 20. The appropriate valves 93 are closed and the vacuum pump 95 is isolated from the system.

In the condenser 45, heat exchange plates 46 are positioned in order to cool the reductant metal vapor introduced therein. The cooling system 60 is operated in a closed loop and maintained at a temperature sufficiently low that reductant metal vapor introduced into the condenser 45 condenses and flows out of the condenser, as will be disclosed. The cooling system 60 includes a cooler 65 as previously described and the pump 62. The coolant exits from the cooler 65 through line 114 which enters the heat exchange plates 46 and leaves through a line 115 which joins the line 116 to interconnect the head tank 62 and the cooler 65. As seen in the schematic of Fig. 1, the heat exchange fluid used in the heating system 50 and the cooling system 60 may

be the same or may be different, as the systems 50 and 60 can be maintained separately or intermixed.

Both the vessel 25 and the condenser 45 are operated at least part of the time under a protective atmosphere of argon or other suitable inert gas from the argon supply 85, the pressure of which is monitored by the transducer 86, the (argon) supply inert gas 85 being connected to the condenser 45 by a line 117, the condenser 45 also being in communication with the vessel 25 by means of the oversized conduit 42. Further, as may be seen, each of the heating system 50 and the cooling system 60 is provided with its own pump, respectively 53 and 63. As suggested in the schematic of Fig. 1, the heating and cooling fluid may, preferably be NaK due to its lower melting point, but not necessarily, and as an alternative could be the same as the reductant metal in either liquid or vapor phase, as disclosed.

After sufficient reductant metal 18 has been removed from the slurry 20, via the filter 27 and the conduit 42, remaining therein is a combination of the titanium product in powder form and salt made during the exothermic reaction in reactor 15. Because the resultant dried cake has a smaller volume than the slurry product 20 introduced, when the movable bottom closure 30 is opened, the dry cake falls from the filter 27 into the collection vessel 35 whereupon the combination of salt and titanium fall into the crusher 38 due to the sloped bottom walls 36. In the event the cake does not readily fall of its own accord, various standard vibration inducing mechanism or a cake breaking mechanism may be used to assist transfer of the cake to the collection vessel 35. The collection vessel 35 as indicated is maintained under an inert atmosphere at about atmospheric pressure, and after the cake passes through the crusher 38 into the exit or outlet 40, the cake passes downwardly through valve 39 onto the conveyor 70. There is a cake spreader or baffle 71 downstream of the valve 39 which spreads the cake so that as it is contacted by a mixture 77 of inert gas, preferably argon, and oxygen flowing counter-current to the direction of the product, the titanium powder is passivated and cooled. Although the conveyor 70 is positioned in Fig. 1 horizontally, it may be advantageous to have the conveyor move upwardly at a slant as a safety measure in the event that closure 30 fails, then excess reductant metal would not flow

toward a water wash. In addition, there may be cost advantages in having the product wash equipment on the same level as the separation equipment.

Cooling and passivating is accomplished in the cooler 79 with blower 75 which blows a cooled argon and oxygen mixture through a conduit 121 to the product, it being seen from the schematic that the counter-current flow of argon and oxygen with the product has the highest concentration of oxygen encountering already passivated and cooled titanium so as to minimize the amount of oxygen used in the passivation process. Oxygen is conducted to the system from a supply thereof 76 through a valve 93 and line 122 and is generally maintained at a concentration of about 0.1 to about 3% by weight. The mixture of passivated titanium and salt is thereafter fed to a wash system not shown. Various flow meters 81 are positioned throughout the system as required, as are pressure control valves 89 and pressure transducers 86. A filter backwash valve 91 is positioned so that the filter 27 can be backwashed when required if it becomes clogged or otherwise requires backwashing. Standard engineering items such as valves 93, vacuum pump 95 and pressure transducers 86 are situated as required. Symbol 100 is used to denote that parallel systems identical or similar to all or a portion of the system 10 illustrated may be operated simultaneously or in sequence.

In the Armstrong process, the production of the metal, alloy or ceramic is continuous as long as the reactants are fed to the reactor. The present invention provides a separation system, apparatus and method which permits the separation to be either continuous or in sequential batches so rapidly switched by appropriate valving as to be as continuous as required. The object of the invention is to provide a separation apparatus, system and method which allows the reactor(s) 15 in a commercial plant to operate continuously or in economic batches. Reduction of the distillation time in vessel 25 is important in order to operate a plant economically, and economics dictate the exact size, number and configuration of separation systems and production systems employed. Although described with respect to Ti powder, the invention applies to the separation of any metal, alloy thereof or ceramic produced by the Armstrong process or other industrial processes.

The heating mechanism shown is by fluid heat exchange, but heaters could also be electric or other equivalent means, all of which are incorporated herein. The bottom closure 30 is shown as hinged and is available commercially. The closure 30 may be clamped when shut and hydraulically moved to the open position; however, sliding closures such as gate valves are available and incorporated herein. Although the reactor 20 is shown separate from the vessel 25, the invention includes engineering changes within the skill of the art, such as but not limited to incorporating reactor 20 into vessel 25. Although vessel 35 is illustrated in one embodiment, the vessel 35 could easily be designed as a pipe. Also, the crusher 38 could be located in vessel 25 or intermediate vessel 25 and vessel 35. Moreover, the cake forming on the filter 27 may be broken up prior to or during or subsequent to removal of the liquid metal therefrom. Similarly, when referring to an inert environment, the invention includes a vacuum as well as an inert gas. An important feature of the invention is the separation of vessels 25 and 35 so the environments of each remain separate. That way, no oxygen can contaminate either vessel.

In one specific example, a reactor 15 producing 2 million pounds per year of titanium powder or alloy powder requires two vessels 25, each roughly 14' high and 7' in diameter with appropriate valving, so that the reactor 15 would operate continuously and when one vessel 25 was filled, the slurry product from the reactor would switch automatically to the second vessel 25. The fill time for each vessel 25 is the same or somewhat longer than the deliquor, distill and evacuation time for vessel 25.

Changing production rates of reactor 15 simply requires engineering calculations for the size and number of vessels 25 and the related equipment and separation systems. The invention as disclosed permits continuous production and separation of metal or ceramic powder, while the specific example disclosed permits continuous separation with two or at most three vessels 25 available for each reactor 15. With multiple reactors 15, the number of vessels 25 and related equipment would probably be between 2 and 3 times the number of reactors.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A method of separating metal powder from a slurry of liquid metal and metal powder and salt, comprising introducing the slurry into a first vessel operated in an inert and/or vacuum environment for separation of liquid metal from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal, transferring the salt and metal powder substantially free of liquid metal to a second vessel operated in an inert environment, and thereafter treating the salt and metal powder to produce passivated metal powder substantially free of salt and liquid metal.

2. The method of claim 1, wherein the inert environment is an argon atmosphere.

3. The method of claim 1, wherein the salt and metal powder are crushed to form clumps having diameters less than about five centimeters prior to passivation.

4. The method of claim 1, wherein the liquid metal is separated from the salt and metal powder in the first vessel both as a liquid and as a vapor.

5. The method of claim 4, wherein the liquid metal vapor from the first vessel is transferred to a condenser operated in an inert environment.

6. The method of claim 4, wherein the liquid metal is an alkali or an alkaline earth metal or mixtures thereof.

7. The method of claim 6, wherein the salt is a halide.

8. The method of claim 7, wherein the metal powder is titanium or a titanium alloy.

9. The method of claim 8, wherein the titanium or titanium alloy is CP 1 to CP 4.

10. The method of claim 9, wherein the metal powder has diameters in the range of from about 0.1 to about 10 microns.

11. The method of claim 1, wherein passivation occurs on a conveyor.

12. The method of claim 11, wherein the metal powder is continuously cooled and passivated.

13. The method of claim 1, wherein the environments of the first and second vessels are protected from contamination by oxygen during the production of metal powder substantially free of salt and liquid metal.

14. A method of separating metal powder from a slurry of liquid metal and metal powder and salt formed by introducing a metal halide vapor subsurface of a liquid metal causing an exothermic reaction producing salt and metal powder with the liquid metal being present in excess of the stoichiometric amount required, comprising introducing the slurry into a first vessel operated in an inert and/or vacuum environment for filtration and vaporization of liquid metal from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal, transferring the liquid metal vapor to a condenser operated in an inert environment to convert the liquid metal vapor to a liquid to be recycled for production of additional metal powder, transferring the salt and metal powder substantially free of liquid metal to a second vessel operated in an inert environment, and thereafter treating the salt and metal powder to produce passivated metal powder substantially free of salt and liquid metal.

15. The method of claim 14, wherein the slurry is heated in the first vessel by contact with a heat exchanger internal to the first vessel having heat exchange fluid pumped therethrough.

16. The method of claim 14, wherein the liquid metal vapor from the first vessel is cooled by contact with heat exchanger internal to the condenser having a heat exchange fluid pumped therethrough.

17. The method of claim 14, wherein the first vessel is heated by both an internal and an external heat exchanger.

18. The method of claim 14, wherein the slurry is introduced into the interior of a candle filter in the first vessel with liquid metal flowing through the candle filter and out of the first vessel.

19. The method of claim 14, wherein the inert environment for the first and second vessels is an argon atmosphere.

20. The method of claim 19, wherein the condenser is operated in an argon atmosphere.

21. The method of claim 14, wherein the environments of the first and second vessels are protected from contamination by oxygen during the production of metal powder substantially free of salt and liquid metal.

22. A system for separating metal powder from a slurry of liquid metal and metal powder and salt formed by introducing a metal halide vapor subsurface of a liquid metal causing an exothermic reaction producing salt and metal powder with the liquid metal being present in excess of the stoichiometric amount required, comprising a first inerted vessel in communication with a heater and a filter for filtering liquid metal from the slurry and for heating liquid metal to vaporize the liquid metal from the salt and metal powder forming a filter cake of salt and metal powder, an inerted condenser in communication with said first vessel for receiving metal vapor and converting same to liquid metal, a second inerted vessel in valved communication with said first inerted vessel for receiving filter cake therefrom; a crusher in or in communication with said second inerted vessel for crushing the filter cake; a cooling and passivating station for receiving crushed filter cake, and a valve mechanism intermediate said first and second vessel and between said second vessel and said cooling and passivating station to prevent air from contaminating said first and second vessels during transfer of filter cake from said first vessel to said cooling and passivating station.

23. The system of claim 22, wherein said heater in communication with said first inerted vessel is interior of said vessel.

24. The system of claim 23, wherein said heater interior of said inerted first vessel is in communication with a source of heat exchange fluid which optionally is dedicated to said heater.

25. The system of claim 22, wherein said filter in communication with said first inerted vessel is interior of said vessel.

26. The system of claim 25, wherein said filter is a filter forming an annulus with said first inerted vessel into which liquid metal flows, and further including a conduit

in communication with said annulus for transferring liquid metal from said first inerted vessel to an inerted liquid metal reservoir.

27. The system of claim 22, wherein said first and second inerted vessels are inerted with argon.

28. The system of claim 27, wherein said condenser is inerted with argon.

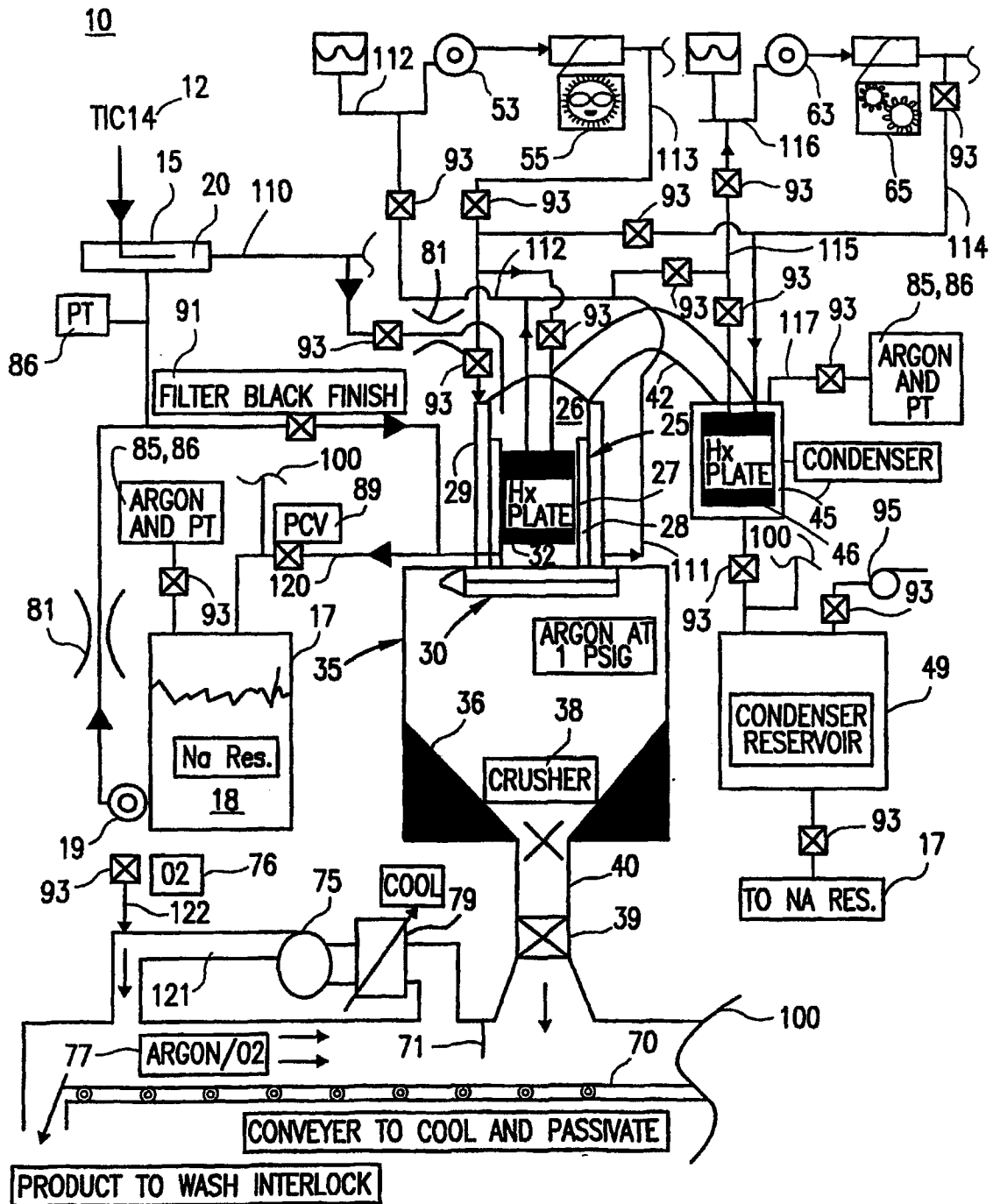
29. The system of claim 28, wherein said inerted condenser is in communication with an argon inerted reservoir for liquid metal formed from condensed metal vapor.

30. The system of claim 22, wherein said condenser is in communication with a source of heat exchange fluid which optionally is dedicated to said condenser.

31. The system of claim 22, wherein said valve intermediate said first and second inerted vessel is hinged to open into said second inerted vessel.

32. The system of claim 22, wherein said first and second vessel are integral.

1/1



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/27649

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B9/02 C22B9/04 C22B34/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 409 797 B2 (ANDERSON RICHARD PAUL ET AL) 25 June 2002 (2002-06-25) cited in the application	1,2, 4-10,14, 19,20
Y	column 4, lines 24-29 and lines 49-55; column 7, lines 32-45	11,12
Y	US 4 379 718 A (GRANTHAM LEROY F ET AL) 12 April 1983 (1983-04-12) abstract; column 6, lines 32-46	11,12
A	US 3 867 515 A (BOHL LESTER E ET AL) 18 February 1975 (1975-02-18)	
A	US 5 437 854 A (WALKER ROY G ET AL) 1 August 1995 (1995-08-01)	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

19 December 2003

Date of mailing of the international search report

02/01/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bjoerk, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/27649

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6409797	B2	17-01-2002	US 5958106 A	28-09-1999
			US 5779761 A	14-07-1998
			US 2002005090 A1	17-01-2002
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A ,B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
			RU 2152449 C1	10-07-2000
			WO 9604407 A1	15-02-1996
US 4379718	A	12-04-1983	AU 543753 B2	02-05-1985
			AU 8346582 A	25-11-1982
			CA 1193447 A1	17-09-1985
			JP 1716294 C	27-11-1992
			JP 3080854 B	26-12-1991
			JP 57194220 A	29-11-1982
US 3867515	A	18-02-1975	NONE	
US 5437854	A	01-08-1995	NONE	

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
3 March 2005 (03.03.2005)

PCT

(10) International Publication Number
WO 2005/019485 A1

(51) International Patent Classification: **C22B 34/12**,
9/02, B01D 29/00

[US/US]; 7680 Steeple Chase Drive, Frankfurt, IL 60423 (US).

(21) International Application Number:
PCT/US2004/027277

(74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar LLC, 125 South Wacker Drive, Suite 2080, Chicago, IL 60606 (US).

(22) International Filing Date: 23 August 2004 (23.08.2004)

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/497,192 22 August 2003 (22.08.2003) US

(71) Applicant (*for all designated States except US*): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

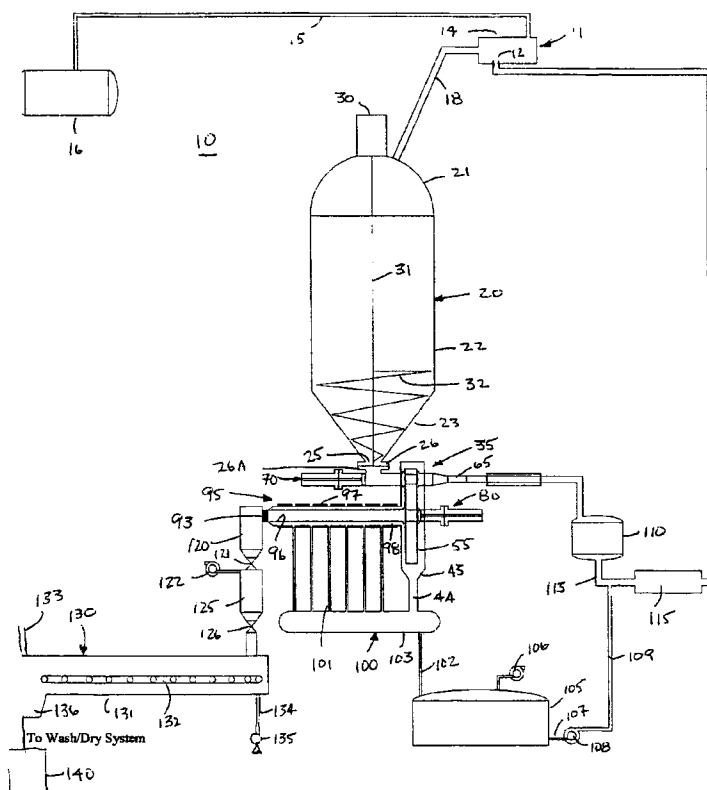
(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **ERNST, William, A.**

[Continued on next page]

(54) Title: INDEXING SEPARATION SYSTEM



(57) Abstract: A method and apparatus are disclosed for continuously separating a metal powder from a slurry of liquid metal and salt and metal powder. Liquid metal is incrementally expressed to form a cake of metal powder and salt and some metal. Then, the incrementally formed cakes are distilled to vaporize metal leaving metal powder and salt substantially free of liquid metal followed by washing the salt from the metal powder and drying the metal powder. Also disclosed are a variety of products made from the metal powder.



European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

Declaration under Rule 4.17:

- of inventorship (Rule 4.17(iv)) for US only

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INDEXING SEPARATION SYSTEM

BACKGROUND OF THE INVENTION

This invention relates to a separation process useful in treating slurries, particularly slurries comprised of metal and non metal particulates such as Ti or Ti alloy powder or particulates, salt, and liquid metal. More particularly, the invention relates to a separation process for a slurry which is produced according to the Armstrong Process as disclosed in each of the three U.S. patents issued thereon, more specifically U.S. patent no. 5,779,761, U.S. patent no. 5,958,106, and U.S. patent no. 6,409,797, the entire disclosures of all three patents being herein incorporated by reference.

Although various metals of controlling the reaction temperature are disclosed in the Armstrong Process, the most commercially advanced method, at the present time, is the use of excess reductant metal, such as sodium, to absorb the heat of reaction during the exothermic reduction of the halide gas, such as titanium tetrachloride to product titanium or a combination of chlorides to produce an alloy. Using an excess of liquid reductant metal, there is produced as reaction products, a powder of the element or alloy to be produced, a particulate salt and excess reductant metal. It should be understood that the scope of this invention is beyond the product of the Armstrong Process and extends to any slurry composed of liquid metal and particulates in which the particulates have to be separated from the liquid metal and thereafter treated. For purposes of brevity only, but not by way of limitation, the description will be in terms of the exothermic reduction of titanium tetrachloride with sodium to produce titanium particles, sodium chloride particles and excess sodium.

During the commercialization of the Armstrong Process, in particular, there is a requirement to handle expeditiously the product from the Armstrong reactor, because the product is formed so quickly the continuous processing thereof has become extremely important. The present invention provides a system and method for handling the product produced by the Armstrong Process such that the Armstrong reactor may be operated continuously to produce 2,000,000,000 pounds per year of elemental metal or alloy while utilizing a single separation vessel and system for the reactor. This is important because it permits the Armstrong reactor to be operated twenty-four hours a day, 7 days a week, economically to produce metal or alloys or any material made by the Armstrong Process as well as applying to handling other slurries as hereinbefore stated.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a continuous method for treating a slurry of liquid metal and particulates.

Another object of the present invention is to provide a continuous method, system and apparatus for separating particulates from a liquid metal slurry containing same.

Yet another object of the present invention is to provide a method of continuously separating a metal powder from a slurry of liquid metal and salt and metal powder, comprising incrementally expressing liquid metal from the slurry to form a cake of metal particulates and salt and some metal, distilling the incrementally formed cakes to vaporize metal leaving metal powder and salt particulates substantially free of liquid metal, washing the salt from the metal powder, and drying the metal powder.

Still another object of the invention is to provide a method of the type set forth comprising introducing a metal halide gas into the liquid phase of a reductant metal to produce a slurry of metal powder and excess reductant metal and a halide salt of the reductant metal, incrementally expressing liquid reductant metal to form a cake, distilling the incrementally formed cakes to vaporize reductant metal leaving metal powder and salt substantially free of reductant metal, passivating the metal powder, washing the salt from the passivated metal powder, and drying the metal powder.

A further object of the present invention is to provide a system of continuously producing metal powder, comprising a reaction chamber for introducing a metal halide gas into the liquid phase of a reductant metal to produce a slurry of metal powder and excess reductant metal and reductant metal halide salt, compression apparatus for incrementally expressing liquid reductant metal to form a cake with some reductant metal, distillation apparatus for heating incrementally formed cakes to separate reductant metal leaving metal powder and salt substantially free of reductant metal, apparatus contacting the metal powder with oxygen or water to passivate same, apparatus washing the salt from the passivated metal, and apparatus for drying the metal powder.

Yet another object of the present invention is to provide a system of continuously producing metal powder, comprising a vessel containing a slurry of metal powder and liquid metal and a metal halide salt, and having an opening through which slurry flows, compression apparatus for incrementally expressing liquid metal from the slurry to form a cake with some liquid metal, a distillation apparatus for heating incrementally formed cakes to vaporize liquid metal leaving metal powder and salt substantially free of liquid metal, apparatus washing the salt

from the metal powder, and apparatus for drying the metal powder.

A final object of the present invention is to provide a method and system of the type set forth in which the dried metal powder is formed into a product which may be one or more of a solid, a powder injection molded part, a powder metal molded part, a powder metallurgy molded part, a part formed by cold isostatic pressing, a part formed by hot isostatic processing, a densified metal powder product, a product formed from melting the metal powder and forming a solid product therefrom, a product formed by cold spraying the metal powder in a gas jet, a product formed by subjecting the metal powder to a laser, a product formed by spheridizing the metal powder in a plasma, a product formed by foaming and sintering the metal powder, a product formed by rolling the metal powder into a plate and sintering, a product formed by preforming the metal powder onto a mandrel and rolling to form tubes, a product formed by drawing the metal powder, a product formed by extruding the metal powder, and a product formed by treating the metal powder.

These and other objects of the present invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be

readily understood and appreciated.

FIGURE 1 is a schematic view of a system for practicing the method of the present invention;

FIG. 2 is an enlarged schematic representation of the product filtering disc portion of the system illustrated in Fig. 1 shown in longitudinal sectional view;

FIG. 2A is a schematic representation of the product filtering disc of the system illustrated in Fig. 2 with an additional converging or equivalent screw conveyor mechanism;

FIG. 3 is a horizontal cross-sectional view of the vessel illustrated in Fig. 2;

FIG. 4 is an alternate embodiment of the system illustrated in Fig. 1; and

FIG. 5 is a schematic representation of a variety of processes and products made by or from powder separated from slurries according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to Figures 1-3, there is disclosed a system 10 for continuously processing a liquid metal slurry containing particulates. In this description, powder and particulates are used interchangeably. More particularly, the system 10 includes a reactor 11 such as, but not limited to the type shown in the Armstrong Process, including a nozzle 12 through which liquid metal flows and having a housing 14 surrounding the nozzle. A gas inlet 15 serves to introduce gas from a source 16 thereof into the liquid metal thereby producing an exothermic reaction as described in the referenced Armstrong patents. The product from the exothermic reaction may be a slurry of a liquid reducing metal, such as sodium, having dispersed therein particles of the element or alloy produced, such as titanium or an alloy thereof, and the reaction product from the gas, which may be sodium chloride or combination of chloride salts, as in the case of sodium and titanium tetrachloride. The slurry leaves

the reactor housing 14 through an outlet 18 and is introduced into a receiving vessel 20 having near the top thereof a dome portion 21 and a cylindrical portion 22 terminating in a frustoconical portion 23 having a discharge outlet 25 at the bottom thereof terminating in a circular flange 26. A motor 30 may be mounted at the top of the vessel 20 connected to an output shaft 31 having an agitator 32 at the bottom of the cylindrical portion 22 or the frustoconical portion 23 as illustrated, for a purpose hereinafter set forth.

Indexing filter system 35, as seen particularly in Fig. 2, is in communication with the vessel 20 and more particularly includes a housing 36, having a top 37, a cylindrical side wall 38 provided with opposed upper apertures 39 and opposed lower apertures 41. The housing 36 is also provided with an outlet 43 having a conduit 44 extending therefrom, for a purpose hereinafter set forth.

An index drive 45 includes a motor 46 having an output shaft 47 in communication with a clutch mechanism 48 connected to an axle 49, the end of which rests in a bearing 51. An aperture 49A is provided in the cylindrical wall 38 to accommodate the axle 49.

An indexing disc 55 is rotatably mounted on the axle 49, the disc having a plurality of longitudinally spaced apart chambers 56 therein, six such chambers being shown for purposes of illustration.

A filter 60, preferably but not necessary a metal wedge wire, is positioned in exit conduit 65 and has a collar 61 maintained in sealing contact with the disc 55 through a spring and pin arrangement 62. The chambers 56 in the disc 55 are also in contact with a collar and spring and pin arrangement in communication with an inlet conduit 63 so as to provide a sealing arrangement for each chamber 56 as it rotates about the axle 49. There is, as illustrated in Fig. 2, a T-shaped conduit 66

having flanges and seals 67 connecting the outlet 25 of the vessel 20 to the indexing disc 55, there being provided a sealing flange 26A (Fig. 1) with the usual seals (not shown) to provide a suitable connection between the vessel 20 and the indexing filter system 35.

Compaction ram assembly 70 is mounted to the housing 36 of the indexing filter system 35 and includes a piston rod 71 having mounted thereon a piston 72. The piston rod 71 is surrounded by a bellows seal 73 and is connected at one end to a suitable drive or motor assembly 74 for longitudinal movement toward and away from the chamber 56, as will hereinafter be described.

A discharge ram assembly 80 is mounted to the housing 36 including a similar piston rod 82, bellows seal 83 and drive motor 84 which is similar to the compaction ram assembly 70. In the illustration of Fig. 2, the discharge ram assembly 80 is rotated for clarity but may be positioned anywhere around the housing 36 in which a chamber 56 is positioned during the indexing of the disc 55, as is well understood by any competent engineer. Moreover, the system 10 of the present invention may also include two or more compaction ram assemblies and two or more discharge ram assemblies, each version being a matter of choice of design, well within the skill of the art. The discharge ram assembly 80 further includes, as did the compaction ram assembly 70, collars 86 and springs and retaining pins 87 to ensure a seal between the discharge ram assembly 80, the indexing disc 55 and the outlet conduit 90 which is surrounded by an outer containment tube or conduit 91, for a purpose hereinafter described.

A cake breaker 93 which may be in the form of a stationary grid or flexible members is positioned at the end of the distillation system 95, as will be explained and for a purpose hereinafter described.

A distillation system 95 is in communication with the outlet conduit 90 of the indexing filter system 35 and includes a longitudinally extending conveyor 96 in a container 98 having a heat exchanger 97 in heat exchange relationship therewith. The distillation system 95 is in communication with a condenser assembly 100 by means of one more tubes 101 extending from the container 98 to a condenser container 103, it being understood that the condenser container 103 is shown for purposes of illustration as an elongated container but may be of any size or shape as determined. The condenser container 103 is also connected by the conduit 44 to the outlet 43 of the housing 36. A conduit 102 provides communication between the condenser assembly 100 and a liquid metal supply 105 in the form of vessel having connected thereto a distillation vacuum pump 106 and an outlet pipe 107. A pump 108 pumps liquid metal from the supply vessel 105 through a conduit 109 to a liquid metal accumulation tank 115. The tank 115 also receives liquid metal from a head tank 110 in communication with the outlet conduit 65 from the indexing filter system 35, the head tank 110 being in communication with the accumulation tank 115 by means of a conduit 113. A heat exchanger 112 may be in heat exchange relationship with the outlet conduit 65 if heat is needed to be added or removed from the liquid metal exiting the indexing filter system 35, as will be explained.

A vessel 120 is positioned in communication with the distillation system 95 and includes a valve 121, the vessel 120 being in communication with a pump 122 which in turn is in communication with a vessel 125 or lock hopper which is also provided with a valve 126 at the bottom thereof. The vessel or lock hopper 125 through valve 126 is in communication with a passivation system 130 which includes a containment vessel 131, a conveyor 132 in communication with a gas inlet conduit 133 and a gas outlet conduit 134 in communication with a pump 135. The

passivation system 130 has an outlet 136, all for a purpose hereinafter set forth.

Operation of the system 10 is as follows. A supply of gas 16 is brought to temperature in a boiler which is meant to be included in the vessel 16 and is transmitted through a conduit or gas inlet pipe 15 into a nozzle 12 through which flows the reductant metal, such as sodium. Sodium is provided from the head tank 110 or supply vessel 105. As is understood, these vessels may be combined into one or may be several, it being within the skill of the art to design the exact combination of parts in the system. Liquid metal pump 105 provides a continuous flow of liquid metal to the nozzle 12 and the amount of liquid metal and gas is adjusted to maintain the temperature in the reactor 11 at a predetermined but generally low temperature of about 400°C. It is understood that various temperatures may be selected as the operating temperature but about 400°C is preferred at the present time. The reaction products in the reactor 11, as previously explained in the Armstrong et al. patents incorporated herein by reference and the illustrated example herein, comprise a slurry of excess sodium, sodium chloride particles and titanium particles. This slurry flows through outlet conduit 18 into the receiving vessel 20. The temperature of the material at this time is still approximately the outlet temperature from the reactor 11 which may be for instance, about 400°C. In the vessel 20, the slurry is stirred in the vessel when the agitator 32 is operated by virtue of the motor 30. The slurry exits the vessel 20 through the discharge outlet 25 thereof into the indexing filter system 35.

Through gravity, the slurry entering the indexing filter system 35 flows into the T-connector 66 and then into inlet conduit 63 through the filter 60 and into the outlet conduit 65. As the liquid sodium flows through the filter 60 which may be for instance, a 125 micron wedge wire filter, the solids concentration increases as liquid

sodium drains. The compaction ram assembly 70 is actuated and the piston 72 drives forwardly into the chamber 56 compressing the material in the conduit 66 thereby expressing liquid metal through the filter 60 until a cake is formed in which most of the liquid metal has been expressed and there remains what could be categorized as wet cake particulate salt and particulate titanium. This cake has sufficient integrity to hold its shape but at the same time still contains some liquid metal. As indicated in the drawing, liquid metal which exits the indexing filter system 35 through the outlet conduit 65 is then recycled to the head tank 110 and moved via the pump 108 back to the nozzle 12 in the reactor 11. After compression by the compaction ram 70 is complete, the motor therefor 74 withdraws the piston 72 and the indexing disc 55 is rotated by the index drive mechanism 45 so as to advance the next chamber 56 into position for another actuation. As is seen from the drawing, because the inlet conduit 66 is connected via gravity to the vessel 20, as soon as the compaction ram 70 withdraws more slurry enters the system. As the disc 55 is rotated as soon as the ram is withdrawn, no slurry material enters the chamber 56 after compaction until the next chamber is in alignment with the compaction ram 70, at which time the aligned chamber 56 fills with the slurry and is thereafter compacted or compressed.

The discharge ram assembly 80 is in alignment or in registry with another chamber 56 of the indexing disc 55 and when the chamber 56 which has the compressed or compacted material therein is in alignment with the discharge ram 80 the piston 82 moves the cake in the chamber 56 into the distillation system 95.

As seen from Fig. 2, there are a plurality of seals 61 and 86 which contain the liquid metal in the appropriate conduit and in its restricted path. However, seals are not necessarily perfect in the real world and although the sealing mechanism in the

conduits are intended to provide a seal for the liquid metal, some inevitably may escape and is collected within the housing 36 and flows out of the outlet 43 and conduit 44 into the condenser assembly 100 for further recycle, as will be explained. Although illustrated with one compaction ram assembly 70 and one discharge ram assembly 80, it is well within the skill of the art to include more than one compaction and/or discharge ram assembly 70, 80.

In the distillation system 95, the particulates from the cake are heated by virtue of the heat exchanger 97, which may be via conduction, convection, induction heating or any other suitable commercial method of heating the powder or particulates moved by the conveyor 96 through the cake breaker 93 to the vessel 120. The cake breaker 93 is shown schematically and may be a fixed series of wires or a variety of other mechanical mechanisms which breaks a compacted particulate matter into a loose friable material. Liquid metal which is vaporized in the distillation system 95 is collection and transmitted via conduits 101 into the condenser assembly 100 and container 103 which is maintained at a sufficiently low temperature to condense the liquid metal vapor into a liquid which is transmitted to storage, such as in head tank 110. As previously described, eventually the liquid metal in the tanks 105 and 110 is recirculated via the pump 108 to the reactor 11 and more particularly the nozzle 12. A valve 121 exists between the vessel 120 and the vessel or lock hopper 125. In addition, pump 122 is in communication with the vessel or lock hopper 125 to ensure no vapors back-up into the system 10 and to evacuate the system if it is necessary to isolate the lock hopper 125 by actuation of the valves 121 and 126. From the lock hopper 125 granular material is transmitted to the passivation system 130 and more particularly to a conveyor 132 which moves within a containment vessel 131 while a passivating gas or liquid is provided through

the gas or water inlet or conduit 133. As illustrated, the particulates move in countercurrent relation to the passivation material but may not be required to do so. Preferably, the passivation fluid is a gas containing a small percentage such as 0.2% by volume oxygen and an inert gas such as argon. The passivated material then moves through outlet 136 to a wash and dry system 140. A pump 135 and conduit 134 exhaust the passivating fluid and recycle same, if desired.

Referring now to Fig. 4, there is shown an alternate embodiment of the present invention in which like numbers have been applied to like parts. The principal difference in the embodiment of Fig. 4 is that the indexing disc 55 as well as the indexing filter system 35 is arranged horizontally instead of vertically so that as slurry drains from the bottom of the vessel 20, liquid reducing metal drains through the filter 60 and a compaction occurs after rotation of the indexing disc 55. Thereafter upon further rotation, the discharge ram assembly 80 is actuated to move the cake into the distillation system 95. Other than the positioning of the indexing disc 55, requiring an indexing between recovering slurry and compaction, the operation of the two systems is identical. Additionally, an advantage of the indexing disc 55 and associated mechanism is that the vessel 20 as well as the conditions therein is isolated from the downstream operations such as the distillation chamber 95 and the passivation station 130. The significance of this is that the conditions in the vessel 20 may be inert or under vacuum or at a specific temperature while the conditions in the distillation station or chamber 95 and/or the passivation station or chamber 130 may be completely different without affecting the upstream conditions in the vessel 20. This isolation of vessel 20 from all downstream conditions provides a significant advantage for the Armstrong process.

Referring now to Fig. 2A, there is shown an alternate embodiment of the present invention in which a variable pitch converging screw conveyor 230 is positioned intermediate the indexing disc 55 and the distillation system 95 to convey solids or semi-solids between the indexing disc 55 and the distillation system 95. The variable pitch converging screw conveyor 230 shown in Fig. 2A includes a housing 90 (the same as previously described) through which passes a shaft 231 having screw flights 232 positioned thereon, in a well known manner. The screw flights 232 may be electrically heated or may be configured to accept a heat exchange fluid flowing therethrough, such as liquid alkali metal or more specifically sodium when used in The Armstrong Process as previously described. An advantage of using a variable pitch converging screw conveyor 230 is that another seal is then maintained between the vessel 20 and the downstream treatment apparatus by the compaction of solids into continuously diminishing volume between adjacent screw flights 32. A variety of mechanical equivalents of the variable pitch converging screw conveyor 230 may be substituted herein and are within the skill of the art and are incorporated in this invention.

On the assumption that a single Armstrong reactor can produce 2,000,000 pounds per year of product, such as titanium or a titanium alloy such as titanium, 6% aluminum and 4% vanadium, the chambers 56 would be 10 inches in diameter and 6 inches in length. Preferably there are 6 such chambers in each disc 55 based on calculations that the slurry and/or gel produced in the Armstrong Process which is approximately 22-23% solids by weight. The indexing disc 55 will be indexed approximately every 11 seconds based on the above-described chambers. Different volume chambers or number of chambers will require different indexing times, but this is well within the skill of the art. Under the present example, the material in the

chamber 56 will be compressed by a factor of 4 so that the cake ejected by the compaction ram assembly 80 will be about 1.5 inches thick and have a solids composition between about 64 and 65 percent by weight.

Referring now to Fig. 5, there is disclosed a schematic representation of the various processes and products made in accordance with the present invention. The reduction box is the Armstrong Process in which an exothermic reduction occurs controlled by the use of constituents taught in the above-mentioned and incorporated Armstrong et al patents. The separation is as previously described herein along with the passivation. The passivated material then is transmitted to a wash and dry assembly 140 in which the salt product, in this specific example, sodium chloride, is removed from the product particulates, in the example titanium or titanium alloy powder.

Referring to Fig. 5, the schematic shows that the powder may be melted to form an ingot or other solid product by a variety of methods such as casting or transmitted to a powder metallurgy process which includes, but is not limited to, for instance isostatic cold processing, hot isostatic processing using pressure to densify the metal powder into a predetermined shape and density. The product may also be produced by cold spraying the metal powder in a gas jet or subjecting the metal powder to a laser or spheridizing the metal powder by plasma. The metal powder may be formed into a foam and thereafter pressed and sintered to form a stable metal foam as is well known in the art. The powder may be pressed onto a mandrel and thereafter rolled into a thin wall tube. Moreover, powder product may be formed by drawing or extruding the metal powder. In the event that product morphology such as the packing fraction, mean size or size distribution needs to be altered, attriting mechanism may be used to change the morphology of the powder, including

the packing fraction or reducing the overall size distribution of the powder.

All these methods of producing product as well as the products formed thereby when combined with the present separation process are included in the present invention.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A method of continuously separating a metal powder from a slurry of liquid metal and salt and metal powder, comprising incrementally expressing liquid metal to form a cake of metal powder and salt and some metal, distilling the incrementally formed cakes to vaporize metal leaving metal powder and salt substantially free of liquid metal, washing the salt from the metal powder, and drying the metal powder.
2. The method of claim 1, wherein the cake is formed by filling a chamber terminated by a filter.
3. The method of claim 2, wherein a gel is formed against the filter.
4. The method of claim 3, wherein there are a plurality of chambers filled seriatim.
5. The method of claim 1, wherein the incrementally formed cakes are introduced into an elongated distillation chamber.
6. The method of claim 4, wherein the elongated distillation chambers are disposed generally horizontally.
7. The method of claim 1 wherein the metal powder is passivated after the cakes are distilled to be substantially free of the liquid metal.
8. The method of claim 1 wherein the liquid metal is an alkali or alkaline earth metal, alloys or mixtures thereof
9. The method of claim 1 wherein the metal powder is Ti or an alloy thereof.
10. The method of claim 4, wherein the metal powder is Ti or an alloy thereof, and the liquid metal is an alkali or alkaline earth metal, alloys or mixtures thereof .

11. The method of claim 10, wherein the Ti alloy is 6% Al and 4% V with the remainder being substantially Ti.
12. The method of claim 1 wherein the salt is a halide.
13. The method of claim 10, wherein the metal powder has Fe present in an amount less than about 0.30% by weight, oxygen present in an amount less than about 0.25% by weight, nitrogen present in an amount less than about 0.03% by weight, carbon present in an amount less than about 0.1% by weight, and hydrogen present in an amount less than 0.015% by weight.
14. A solid formed from the metal powder made from the method of claim 1
15. A product made from the method of claim 1
16. A product made from the method of claim 13.
17. A product made from the solid of claim 14.
18. The method of claim 1, and further comprising powder injection molding the metal powder to form a product.
19. The method of claim 1, and further comprising forming a product by powder metallurgy with the metal powder.
20. The method of claim 1, and further comprising forming a product by cold isostatic processing the metal powder.
21. The method of claim 1, and further comprising forming a product by hot isostatic processing the metal powder.
22. The method of claim 1, and further comprising forming a product by molding the metal powder into a predetermined shape and exerting sufficient pressure to densify the metal powder.

23. The method of claim 1, and further comprising forming a product by melting the metal powder and forming a solid product therefrom.
24. The method of claim 1, and further comprising forming a product by cold spraying the metal powder in a gas jet.
25. The method of claim 1, and further comprising forming a product by subjecting the metal powder to a laser.
26. The method of claim 1, and further comprising forming a product by spheridizing the metal powder in a plasma.
27. The method of claim 1, and further comprising forming a product by forming foam from pressing and sintering the metal powder.
28. The method of claim 1, and further comprising forming a product by rolling the metal powder into plate and sintering.
29. The method of claim 1, and further comprising forming a product by preforming the metal powder onto a mandrel and rolling into a thinner wall tube.
30. The method of claim 1, and further comprising forming a product by drawing the metal powder.
31. The method of claim 1, and further comprising forming a product by extruding the metal powder.
32. The method of claim 1, and further comprising forming a product by attriting the metal powder to provide one or more of increasing the packing fraction, reducing the mean size or reducing the size distribution.

33. A method of continuously producing metal powder, comprising introducing a metal halide gas into the liquid phase of a reductant metal to produce a slurry of metal powder and excess reductant metal and a halide salt of the reductant metal, incrementally expressing liquid reductant metal to form a cake, distilling the incrementally formed cakes to vaporize reductant metal leaving metal powder and salt substantially free of reductant metal, passivating the metal powder, washing the salt from the passivated metal powder, and drying the metal powder.

34. The method of claim 33, wherein the reductant metal is an alkali or alkaline earth metal, alloys or mixtures thereof.

35. The method of claim 34, wherein the halide is a chloride.

36. The method of claim 35, wherein the metal powder is Ti or a Ti alloy.

37. The method of claim 36, wherein a gel is formed from the slurry before the cake is formed.

38. The method of claim 33, wherein the incrementally formed cakes are introduced into an elongated distillation chamber .

39. The method of claim 38, wherein the cake is formed in a rotatable chamber in communication in one position with the slurry and in another position with the distillation chamber.

40. The method of claim 39, wherein the rotatable chamber is in an indexing disk mounted for rotation about a substantially horizontal axis and the distillation chamber is positioned substantially horizontally.

41. The method of claim 40, wherein there are plurality chambers circumferentially positioned around the indexing disk.

42. The method of claim 41, wherein a horizontally disposed ram compresses the slurry to form a cake and a horizontally disposed ram transports the cake from the rotatable chamber to the distillation chamber.

43. The method of claim 42, wherein the passivating is accomplished with oxygen or water.

44. The method of claim 43, wherein the metal powder is Ti or a Ti alloy.

45. The method of claim 44, and further comprising forming the Ti or Ti alloy powder into a solid.

46. The method of claim 33, wherein the metal powder is Ti or a Ti alloy and is formed into a product by powder injection molding.

47. The method of claim 39, and further comprising forming the metal powder into a solid of Ti or a Ti alloy.

48. A system of continuously producing metal powder, comprising a vessel containing a slurry of metal powder and liquid metal and a metal halide salt, and having an opening through which slurry flows, compression apparatus for incrementally expressing liquid metal from the slurry to form a cake with some liquid metal, a distillation apparatus for heating incrementally formed cakes to vaporize liquid metal leaving metal powder and salt substantially free of liquid metal, apparatus washing the salt from the metal powder, and apparatus for drying the metal powder.

49. The system of claim 48, and further comprising a plurality of chambers for receiving slurry and discharging cake.

50. The system of claim 49, wherein the chambers are circumferentially spaced around a rotatable disk.

51. The system of claim 50, wherein said compression apparatus includes a ram for compressing the slurry against a filter to form a cake.

52. The system of claim 51 and further including a ram for transporting the cake to said distillation apparatus.

53. The system of claim 52, and further including a conveyor for transporting the distilled cakes to said washing apparatus.

54. The system of claim 53, and further including an enclosed conveyor for passing the distilled cake in contact with a gas containing oxygen to passivate the metal powder in the cake.

55. The system of claim 54, wherein the metal powder is Ti or a Ti alloy.

56. The system of claim 55, wherein the Ti alloy contains 6% Al and 4% V.

57. The system of claim 55, and further comprising apparatus for converting the Ti or Ti alloy powder into a solid.

58. A system of continuously producing metal powder, comprising a reaction chamber for introducing a metal halide gas into the liquid phase of a reductant metal to produce a slurry of metal powder and excess reductant metal and reductant metal halide salt, compression apparatus for incrementally expressing liquid reductant metal to form a cake with some reductant metal, distillation apparatus for heating incrementally formed cakes to separate reductant metal leaving metal powder and salt substantially free of reductant metal, apparatus contacting the metal powder with oxygen or water to passivate same, apparatus washing the salt from the passivated metal, and apparatus for drying the metal powder.

59. The system of claim 58, wherein a motor is operably connected to said compression apparatus for indexing a portion thereof.

60. The system of claim 59, wherein said compression apparatus further includes a rotatable disk operably connected to said motor and having a plurality of circumferentially spaced apart chambers each being aligned in one position with a filter and in another position with said distillation apparatus.

61. The system of claim 60, wherein said compression apparatus includes a ram for compressing the slurry against said filter to form a cake.

62. The system of claim 61, and further including a ram for transporting the cake to said distillation apparatus.

63. The system of claim 62, wherein said rotatable disk is positioned to rotate about a substantially horizontal axis and said ram for compression and said ram for transporting are positioned substantially horizontally.

64. The system of claim 63, wherein the filter is stationary.

65. The system of claim 64, and further comprising a collection vessel in communication with said compression apparatus and said distillation apparatus to recover reductant metal.

66. The system of claim 65, wherein the reductant metal is Na and the metal halide gas is TiCl_4 or includes TiCl_4 .

67. The method of claim 1, wherein the cake of metal powder and salt and some metal forms a substantially gas-tight seal.

68. The system of claim 48, wherein said compression apparatus forms a seal with the cake therein to isolate said vessel containing the slurry from said distillation apparatus.

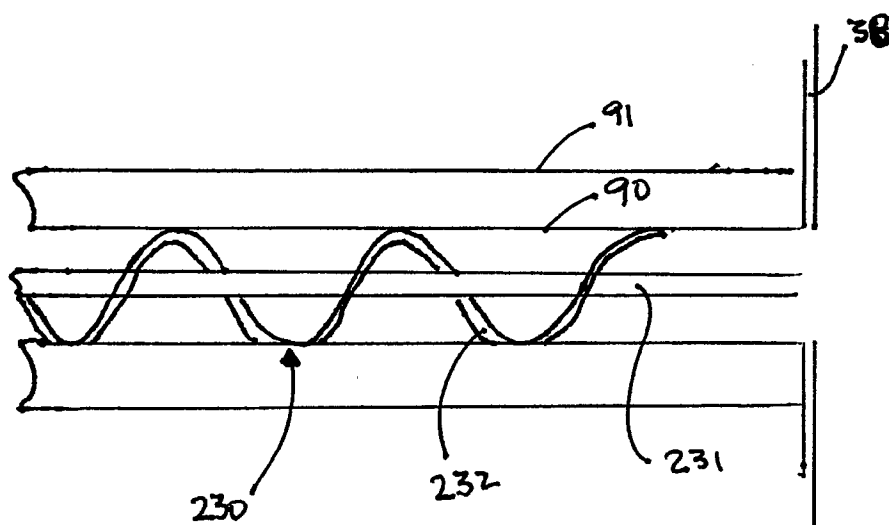


FIGURE 2A

Figure 3

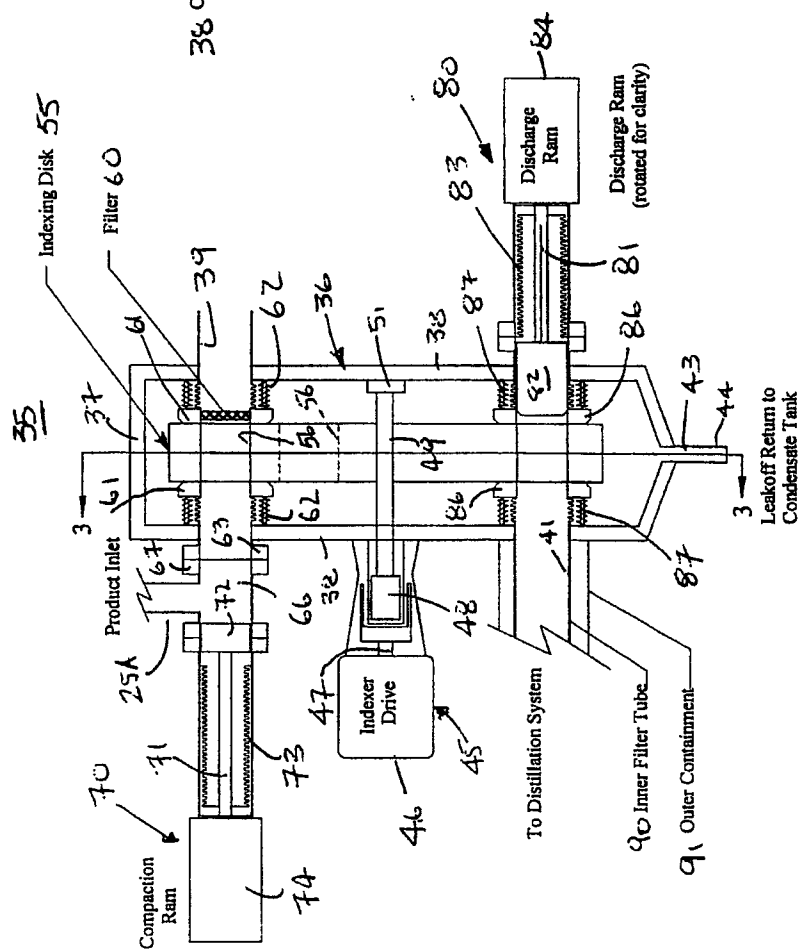


Figure 2

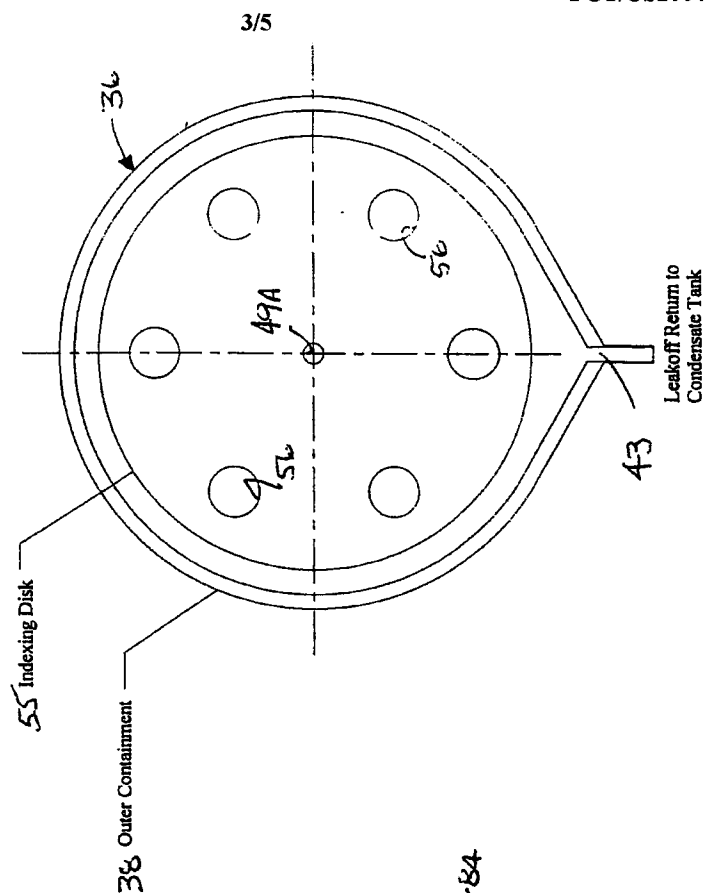
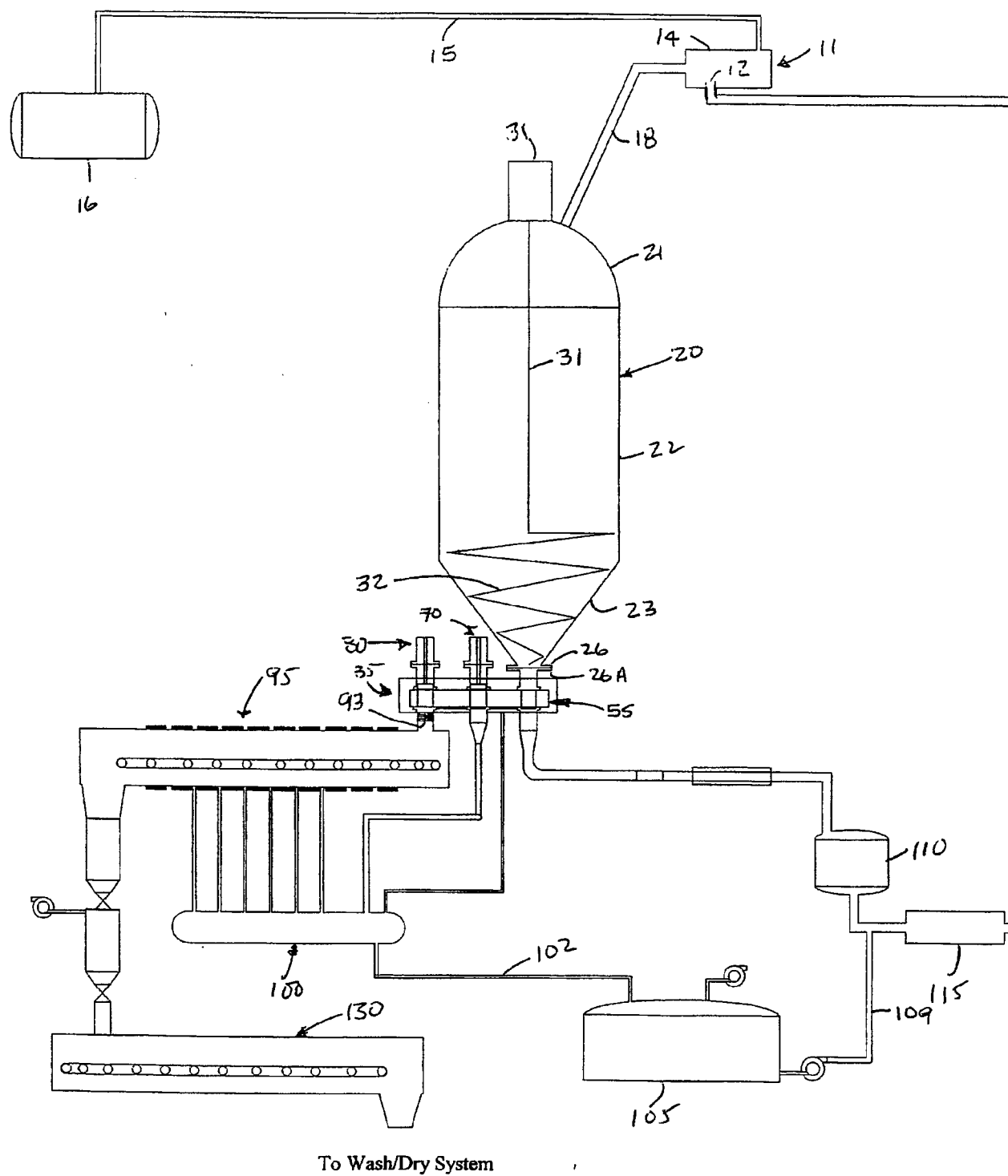


Figure 4



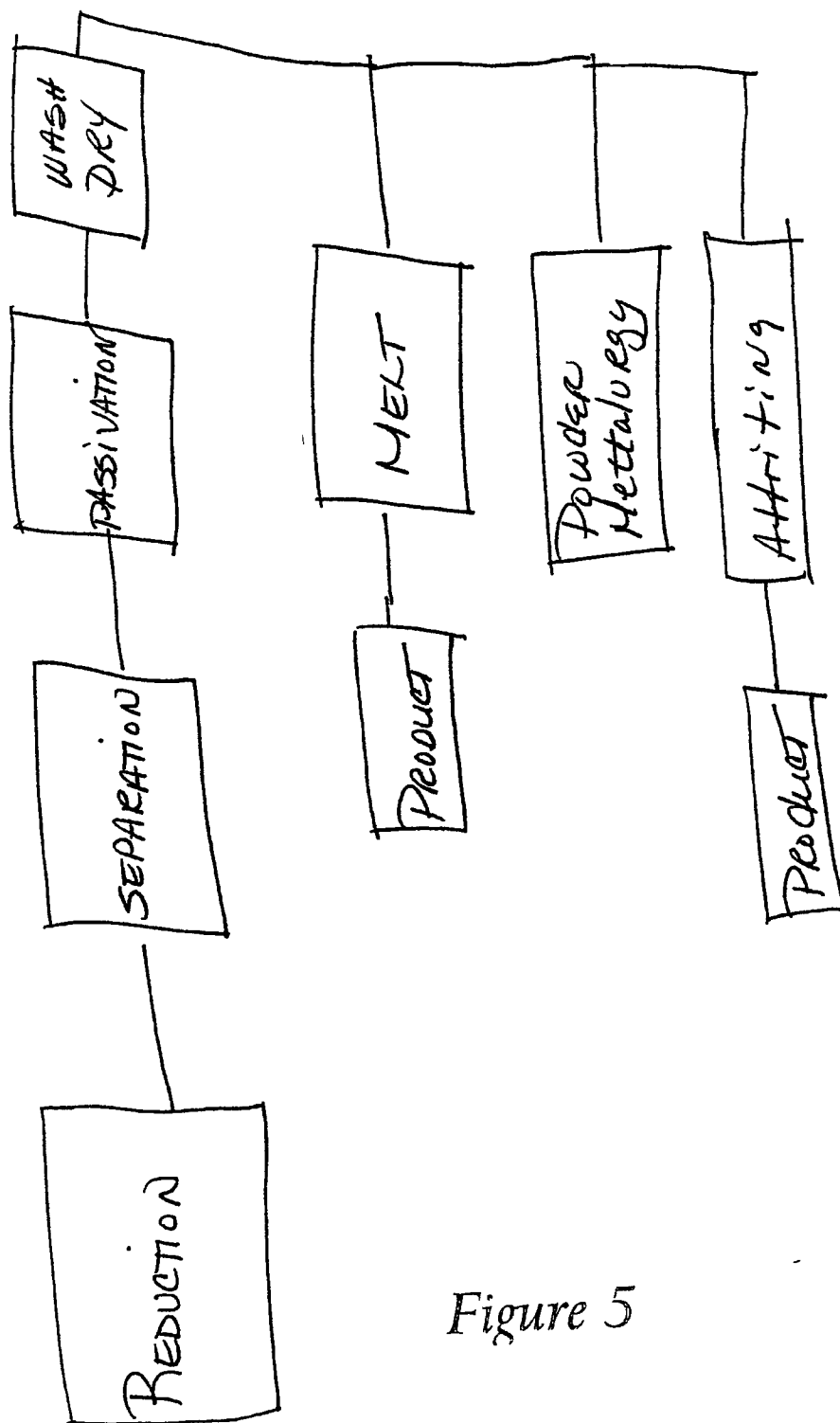


Figure 5

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/027277

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B34/12 C22B9/02 B01D29/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/005090 A1 (ANDERSON RICHARD PAUL ET AL) 17 January 2002 (2002-01-17)	14-17
Y	sections 0022 and 0025; claim 4	1-68
X	US 2 882 143 A (SCHMIDT CHARLES L ET AL) 14 April 1959 (1959-04-14)	14-17
Y	column 2, lines 10-17; column 5, line 63 - column 6, line 15; column 9, lines 33-40	1-68
Y	US 1 771 928 A (HANS JUNG) 29 July 1930 (1930-07-29)	2-4, 39-42, 49-52, 59-64
	page 1, lines 37-43; page 2, lines 27-35	
Y	US 2003/145682 A1 (BORYS STANLEY S ET AL) 7 August 2003 (2003-08-07)	2,37
	Title	
	----- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

1 December 2004

Date of mailing of the international search report

30/12/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bjoerk, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/027277

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	UPADHYAYA G.S.: "Powder Metallurgy Technology" 1997, CAMBRIDGE INTERNATIONAL SCIENCE PUBLISHING, , UK , XP002308396 page 42 - page 67	18-32, 45-47, 57
Y	LU L, FUH J.Y.H. AND WONG Y.S.: "Laser-induced materials and processes for rapid prototyping" 2001, KLUWER ACADEMIC PUBLISHERS , USA , XP002308397 pages 153-154	25
X,P	WO 2004/028655 A (ARMSTRONG DONN ; JACOBSEN LANCE (US); ANDERSON RICHARD (US); INTERNAT) 8 April 2004 (2004-04-08) Claims	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/027277

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002005090 A1	17-01-2002	US 5958106 A	28-09-1999
		US 5779761 A	14-07-1998
		US 2002148327 A1	17-10-2002
		US 2002152844 A1	24-10-2002
		US 2004166045 A1	26-08-2004
		US 2003145682 A1	07-08-2003
		US 2003061907 A1	03-04-2003
		AU 686444 B2	05-02-1998
		AU 3320195 A	04-03-1996
		BR 9508497 A	23-12-1997
		CA 2196534 A1	15-02-1996
		CN 1161064 A ,B	01-10-1997
		DE 69521432 D1	26-07-2001
		DE 69521432 T2	29-05-2002
		EP 0777753 A1	11-06-1997
		ES 2161297 T3	01-12-2001
		JP 10502418 T	03-03-1998
		JP 3391461 B2	31-03-2003
		KR 241134 B1	02-03-2000
		NO 970444 A	26-03-1997
		RU 2152449 C1	10-07-2000
		WO 9604407 A1	15-02-1996
US 2882143 A	14-04-1959	DE 1054720 B	09-04-1959
		FR 1098878 A	23-08-1955
US 1771928 A	29-07-1930	FR 664108 A	05-09-1929
		GB 322091 A	28-11-1929
US 2003145682 A1	07-08-2003	US 2002152844 A1	24-10-2002
		US 5779761 A	14-07-1998
		US 5958106 A	28-09-1999
		US 2004166045 A1	26-08-2004
		US 2002148327 A1	17-10-2002
		US 2003061907 A1	03-04-2003
		US 2002005090 A1	17-01-2002
		AU 686444 B2	05-02-1998
		AU 3320195 A	04-03-1996
		BR 9508497 A	23-12-1997
		CA 2196534 A1	15-02-1996
		CN 1161064 A ,B	01-10-1997
		DE 69521432 D1	26-07-2001
		DE 69521432 T2	29-05-2002
		EP 0777753 A1	11-06-1997
		ES 2161297 T3	01-12-2001
		JP 10502418 T	03-03-1998
		JP 3391461 B2	31-03-2003
		KR 241134 B1	02-03-2000
		NO 970444 A	26-03-1997
		RU 2152449 C1	10-07-2000
		WO 9604407 A1	15-02-1996
WO 2004028655 A	08-04-2004	WO 2004028655 A2	08-04-2004

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
10 March 2005 (10.03.2005)

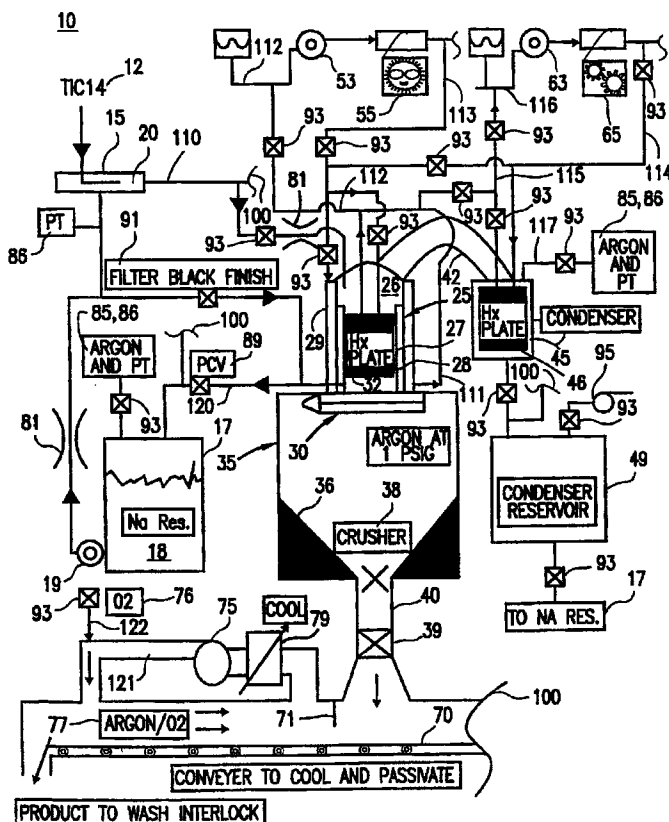
PCT

(10) International Publication Number
WO 2005/021807 A2

- (51) International Patent Classification⁷: **C22B 9/00**
- (21) International Application Number:
PCT/US2004/028553
- (22) International Filing Date:
2 September 2004 (02.09.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
PCT/US03/27649
2 September 2003 (02.09.2003) US
60/499,857 3 September 2003 (03.09.2003) US
PCT/US03/27653
3 September 2003 (03.09.2003) US
PCT/US03/27647
3 September 2003 (03.09.2003) US
- (71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US]; 20634 W. Gaskin Drive, Lockport, IL 60441 (US).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **ARMSTRONG, Donn, Reynolds** [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). **ANDERSON, Richard, P.** [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). **BORYS, Stanley, S.** [US/US]; 372 Walnut, Elmhurst, IL (US). **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US). **KOGUT, Dariusz** [US/US]; 17825 Greenwood Drive, Tinley Park, IL 60477 (US).
- (74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar, LLC., 125 South Wacker Drive, suite 2080, Chicago, IL 60606 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,

[Continued on next page]

(54) Title: SEPARTION SYSTEM, METHOD AND APPARATUS



(57) Abstract: A system, method and apparatus for treating a slurry of liquid metal and solid particles is disclosed using various combinations of vacuum distillation and transfer with hot inert gas. Various mechanisms are disclosed for sealing inerted or vacuum chambers to prevent oxygen infiltration



CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,

SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

SEPARATION SYSTEM, METHOD AND APPARATUS

RELATED APPLICATIONS

This application, pursuant to 35 U.S.C. Section No.119(e) and any other applicable provision of Title 35 U.S.C., claims the priority benefit of U.S. Provisional Application Serial No. 60/499,857, Filed September 3, 2002 entitled: SEPARATION SYSTEM, METHOD AND APPARATUS and PCT Application Serial No. PCT/US03/027649 filed September 2, 2003 entitled SEPARATION SYSTEM AND PROCESS by Richard Armstrong and Lance Jacobsen and of U.S. Provisional Application Serial No. 60/497,192 filed August 22, 2003 entitled INDEXING SEPARATION SYSTEM by William A. Ernst and PCT patent application Serial No PCT/US03/027653 filed September 3, 2003 entitled: FILTER CAKE TREATMENT APPARATUS AND METHOD by Richard Anderson, Donn Armstrong and Lance Jacobsen and PCT Application Serial PCT/US03/027647 filed September 3, 2003 entitled: FILTER EXTRACTION MECHANISM by Richard Anderson, Donn Armstrong and Lance Jacobsen.

BACKGROUND OF THE INVENTION

This invention relates to a separation system, method and apparatus useful for separating the slurry produced by Armstrong method as disclosed and claimed in U.S. Patents 5,779,761; 5,958,106 and 6,409,797, the disclosures of each and every one of the above-captioned patents are incorporated by reference.

Although various metals of controlling the reaction temperature are disclosed in the Armstrong Process, the most commercially advanced method, at the present time, is the use of excess reductant metal, such as sodium, to absorb the heat of reaction during the exothermic reduction of the halide gas, such as titanium tetrachloride to product titanium or a

combination of chlorides to produce an alloy. Using an excess of liquid reductant metal, there is produced as reaction products, a powder of the element or alloy to be produced, a particulate salt and excess reductant metal. It should be understood that the scope of this invention is beyond the product of the Armstrong Process and extends to any slurry composed of liquid metal and particulates in which the particulates have to be separated from the liquid metal and thereafter treated. For purposes of brevity only, but not by way of limitation, the description will be in terms of the exothermic reduction of titanium tetrachloride with sodium to produce titanium particles, sodium chloride particles and excess sodium.

During the commercialization of the Armstrong Process, in particular, there is a requirement to handle expeditiously the product from the Armstrong reactor, because the product is formed so quickly the continuous processing thereof has become extremely important. The present invention provides a system and method for handling the product produced by the Armstrong Process such that the Armstrong reactor may be operated continuously to produce 2,000,000,000 pounds per year of elemental metal or alloy while utilizing a single separation vessel and system for the reactor. This is important because it permits the Armstrong reactor to be operated twenty-four hours a day, 7 days a week, economically to produce metal or alloys or any material made by the Armstrong Process as well as applying to handling other slurries as hereinbefore stated.

In the production of a metal or alloy or other elemental material as described in the above-referenced patents, a slurry is produced which if filtered provides a filter cake in the form of a gel. The slurry has a solids fraction which depends in large part on the amount of excess reductant metal used to control the steady-state temperatures at which the reaction runs. As liquid metal drains through the filter to build the filter cake, a gel is formed from which particles do not settle, unless the gel is broken, such as by mechanical disturbance or

other means. The gel when formed includes the metal particles formed during the reduction, the salt particles formed during the reduction and interstitial liquid metal. The liquid metal in the gel has to be removed by way of distillation with or without a vacuum or by contact with a hot sweep gas, preferably inert to the constituents of the gel with or without a vacuum or any combination thereof.

Summary of the Invention

A principal object of the invention is to provide a separation system, method and apparatus for the Armstrong process disclosed in the '761, '106 and '797 patents;

Another object of the invention is to provide a continuous separation system.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

Brief Description of the Drawings

Figure 1 is a schematic illustration of the separation system of the present invention.

FIG. 2 is a schematic view of a system for practicing the method of the present invention;

FIG. 3 is an enlarged schematic representation of the product filtering disc portion of the system illustrated in Fig. 2 shown in longitudinal sectional view;

FIG. 4 is a horizontal cross-sectional view of the vessel illustrated in Fig. 3

FIG. 5 is an alternate embodiment of the system illustrated in Fig. 2 and

FIG. 6 is a schematic representation of a variety of processes and products made by or from powder separated from slurries according to the present invention.

FIG. 7 is a graph of pressure rise versus time for a flat plate filter nutsche runs;

FIG. 8 shows data for various temperatures as a function of time and pressure;

FIG. 9 shows a schematic of the filter trap for the above example; and

FIG. 10 shows a schematic of another embodiment of the filter trap of Fig. 3.

FIG. 11 is a schematic diagram showing the two vessels and an embodiment of the transfer mechanism therebetween;

FIG. 12 is a schematic of an alternate embodiment of the present invention; and

FIG. 13 is a schematic illustration of yet another embodiment of the present invention; and

FIG. 14 is a schematic representation of a separation system incorporating features of Figs. 1-13.

Detailed Description of the Invention

The system 10 of the present invention deals with the separation of a metal, alloy or ceramic product, such as titanium, for example only, from the reaction products in the Armstrong process. Although the Armstrong process is applicable to a wide variety of exothermic reactions, it is principally applicable to metals, mixtures, alloys and ceramics disclosed in the above-mentioned patents. The product of Armstrong process is a slurry of excess reductant metal, product metal and alloy or ceramic and salt produced from the reaction. This slurry has to be separated so that various parts of it can be recycled and the produced metal, alloy or ceramic separated and passivated if necessary.

Turning now to the schematic illustration of the system and process of the present invention illustrated in Fig. 1, there is disclosed in the system 10 a source of, for illustration purposes only, titanium tetrachloride 12 which is introduced into a reactor 15 of the type hereinbefore disclosed in the Armstrong process. A supply tank or reservoir 17 with a supply of sodium (or other reductant) 18 is transferred by a pump 19 to the reactor 15 wherein a

slurry product 20 of excess reductant and metal, alloy or ceramic, and salt is produced at an elevated temperature, all as previously described in the incorporated patents.

The slurry product 20 is transferred to a vessel 25 which is in the illustration dome-shaped, but not necessarily of that configuration, the vessel 25 having an interior 26 into which the slurry product 20 is introduced. A filter 27, preferably but not necessarily cylindrical, is positioned within the interior 26 and defines an annulus 28, the slurry product 20 being received inside the cylindrical filter 27. An annular heat exchanger 29 is positioned around the vessel 25, all for a purpose hereinafter disclosed.

The vessel 25 further includes a moveable bottom closure 30. Heat exchange plates 32 are connected as will hereinafter be described to an isolated heating system 50. A collection vessel 35 is positioned below the vessel 25 and is sealed therefrom by the moveable bottom closure 30. The collection vessel 35 has an inwardly sloping bottom surface 36 which leads to a crusher 38 and a valve 39 in the outlet 40 of the collection vessel 35.

Finally, a vapor conduit 42 interconnects the top of the vessel 25 and particularly the interior 26 thereof with a condenser vessel 45, the condenser vessel having a heat exchange plate 46 connected, as hereinafter described, to an isolated cooling system 60. The condenser 45 is connected to a condenser reservoir 49, the condensate collected therein being routed to the sodium supply tank or reservoir 17.

The isolated heating system 50 includes a head tank 52 for the heating fluid which is moved by pump 53 to the heater 55 as will be hereinafter described, connected to both the heat exchanger 29 surrounding the vessel 25 and the heat exchange plates 32 interior of the vessel 25. The isolating cooling system 60 also is provided with a head tank 62, a pump 63

and a cooler 65 which serves to cool the cooling fluid circulated in an isolated loop to the cooling plates 46 as will be hereinafter set forth.

Below the valve 39 and the collection vessel 35 is a product conveyor 70 having a baffle or cake spreader 71 extending downwardly toward the conveyor 70. The conveyor 70 onto which the produced metal, alloy or ceramic and salt are introduced from the collection vessel 35, after removal of the excess reductant metal, is contacted with a counter current flow of gas, preferably but not necessarily oxygen and argon, 77 from a blower 75 in communication with a supply 76 of oxygen and the supply of inert gas such as argon. The heat exchanger 79 is in communication with the blower 75 so as to cool the oxygen/argon mixture 77 as it flows in counter current relationship with the produced metal, alloy or ceramic on the conveyor 70, thereby to contact the product particulates with oxygen to inert the produced metal, alloy or ceramic when required but not so much as to contaminate the produced material.

As indicated in the flow sheet of Fig. 1, there are a plurality of flow meters 81 distributed throughout the system, as required and as well known in the engineering art. There are pressure transducers 86 and pressure control valves 89 where required, all within the engineering skill of the art. A back filter valve 91 is provided in order to flush the filter 27 if necessary. Additionally, a variety of standard shut-off valves 93 are positioned within the loop, hereinafter to be explained and as required. A vacuum pump 95 is used to draw a vacuum in the vessel 25, as will be explained, and the symbol indicated by reference numeral 100 indicates that a plurality of the same or similar systems may be operating at any one time, it being remembered that the enclosed figure is for a single reactor 15 and one separation vessel 25, wherein as in a commercial production plant, a plurality of reactors 15 may be

operating simultaneously each reactor 15 may have more than one separation vessel 25, all depending on engineering economics and ordinary scale up issues.

Product 20 from the reactor 15 exits through line 110 and enters vessel 25 at the top thereof. Although line 110 is shown entering above the filter 27, preferably the line 110 and filter 27 are positioned so that slurry 20 is introduced below the top of filter 27 or in the center of the filter or both. As described in the previously incorporated patents, the slurry product 20 consists of excess reductant metal, salt formed by the reaction and the product of the reaction which in this specific example is titanium existing as solid particles. The product 20 in slurry form from the reactor 15 is at an elevated temperature depending on the amount of excess reductant metal present, the heat capacity thereof and other factors in the reactor 15 during operation of the Armstrong process. In the vessel 25 is a filter 27 which occupies a portion of the interior 26 of the vessel 25, the interior optionally being heated with the annular heat exchanger 29. The slurry product 20 is directed to the interior of the filter 27 where the slurry contacts the heat exchange plates 32.

In the heating system 50, the heat exchange fluid in the plates 32 pass with the heat exchange fluid from the annular heat exchanger 29 through line 111 to the line 112 which connects the heat exchange medium supply in the head tank 52 to the heat exchanger 55. Fluid moves from the heater 55 through the heat exchange plates 32 by means of the pump 53 as the heated heat exchange fluid flows out of the heat exchanger 55 through line 113 and back into the heat exchange plates 32 and/or the annular heat exchanger 29. Because the heating system 50 is a closed loop, the heat exchange fluid may or may not be the same as the reductant metal used in the reactor 15. NaK is shown as an example because of the low melting point thereof, but any other suitable heat exchange fluid may be used. Suitable valves 93 control the flow of heat exchange fluid from the heater 55 to either or both of the

heat exchanger 29 and plates 32. Preferably, the plates 32 are relatively close together, on the order of a few inches, to provide more heat to the cake which forms as excess reductant metal vaporizes. Moreover, closer plates 32 reduce the path length the heat has to travel and the path length the excess reductant metal vapor travels through the forming cake, thereby to reduce the time required to distill and remove excess reductant metal from the vessel 25. Exact spacing of the plates 32 depends on a number of factors, including but not limited to, the total surface area of the plates, the heat transfer coefficient of the plates, the amount of reductant metal to be vaporized and the temperature differential between the inside and the outside of the plates.

When the slurry product 20 comes out of the reactor 15, it is at a pressure at which the reactor 15 is operated, usually up to about two atmospheres. The product slurry 20 enters the inside of filter 27 under elevated pressure and gravity results in the liquid reductant metal being expressed through the filter 27 into the annular space 28 and fed by the line 120 into the reservoir 17. The driving force for this portion of the separation is gravity and the pressure differential between the reactor 15 and the inlet pressure of pump 19. If required the annulus 28 may be operated under vacuum to assist removal of liquid reductant metal, or the pressure in vessel 25 may be increased during the deliquoring of the reductant metal. After sufficient liquid metal has drained through the filter 27 by the aforementioned process, the PCV valve 89 is closed and other valves 93 are closed to isolate vessel 25 and then the valve 93 to the vacuum pump 95 is opened, whereupon a vacuum is established in the interior 26 of vessel 25. Heating fluid (liquid or vapor, for instance Na vapor) is directed into the heat exchanger plates 32 to boil the remaining reductant metal 18 producing a filter cake. The temperature in vessel 25 is elevated sufficiently to vaporize remaining liquid metal reductant 18 therein which is drawn off through conduit 42 to the condenser 45. The conduit 42 is required to be

relatively large in diameter to permit rapid evacuation of the interior 26 of the vessel 25.

Because the pressure drop between the vessel 25 and the condenser 45, during vaporization of the reductant metal 18 is low, the specific volume is high and the mass transfer low, requiring a large diameter conduit 42. Boiling the reductant metal on the shell side is accomplished by heat exchange with a heated fluid on the tube side.

The annular heat exchanger 29 is optionally operated to maintain the expressed liquid in the annulus 28 at a sufficient temperature to flow easily and/or to provide additional heat to the vessel 25 to assist in vaporization of excess reductant metal from the interior 26 thereof. After liquid metal reductant vapor has been removed from the interior 26 of the vessel 25, a filter cake remains from the slurry 20. The appropriate valves 93 are closed and the vacuum pump 95 is isolated from the system.

In the condenser 45, heat exchange plates 46 are positioned in order to cool the reductant metal vapor introduced thereinto. The cooling system 60 is operated in a closed loop and maintained at a temperature sufficiently low that reductant metal vapor introduced into the condenser 45 condenses and flows out of the condenser, as will be disclosed. The cooling system 60 includes a cooler 65 as previously described and the pump 62. The coolant exits from the cooler 65 through line 114 which enters the heat exchange plates 46 and leaves through a line 115 which joins the line 116 to interconnect the head tank 62 and the cooler 65. As seen in the schematic of Fig. 1, the heat exchange fluid used in the heating system 50 and the cooling system 60 may be the same or may be different, as the systems 50 and 60 can be maintained separately or intermixed.

Both the vessel 25 and the condenser 45 are operated at least part of the time under a protective atmosphere of argon or other suitable inert gas from the argon supply 85, the pressure of which is monitored by the transducer 86, the (argon) supply inert gas 85 being

connected to the condenser 45 by a line 117, the condenser 45 also being in communication with the vessel 25 by means of the oversized conduit 42. Further, as may be seen, each of the heating system 50 and the cooling system 60 is provided with its own pump, respectively 53 and 63. As suggested in the schematic of Fig. 1, the heating and cooling fluid may, preferably be NaK due to its lower melting point, but not necessarily, and as an alternative could be the same as the reductant metal in either liquid or vapor phase, as disclosed.

After sufficient reductant metal 18 has been removed from the slurry 20, via the filter 27 and the conduit 42, remaining therein is a combination of the titanium product in powder form and salt made during the exothermic reaction in reactor 15. Because the resultant dried cake has a smaller volume than the slurry product 20 introduced, when the movable bottom closure 30 is opened, the dry cake falls from the filter 27 into the collection vessel 35 whereupon the combination of salt and titanium fall into the crusher 38 due to the sloped bottom walls 36. In the event the cake does not readily fall of its own accord, various standard vibration inducing mechanism or a cake breaking mechanism may be used to assist transfer of the cake to the collection vessel 35. The collection vessel 35 as indicated is maintained under an inert atmosphere at about atmospheric pressure, and after the cake passes through the crusher 38 into the exit or outlet 40, the cake passes downwardly through valve 39 onto the conveyor 70. There is a cake spreader or baffle 71 downstream of the valve 39 which spreads the cake so that as it is contacted by a mixture 77 of inert gas, preferably argon, and oxygen flowing counter-current to the direction of the product, the titanium powder is passivated and cooled. Although the conveyor 70 is positioned in Fig. 1 horizontally, it may be advantageous to have the conveyor move upwardly at a slant as a safety measure in the event that closure 30 fails, then excess reductant metal would not flow toward a water wash.

In addition, there may be cost advantages in having the product wash equipment on the same level as the separation equipment.

Cooling and passivating is accomplished in the cooler 79 with blower 75 which blows a cooled argon and oxygen mixture through a conduit 121 to the product, it being seen from the schematic that the counter-current flow of argon and oxygen with the product has the highest concentration of oxygen encountering already passivated and cooled titanium so as to minimize the amount of oxygen used in the passivation process. Oxygen is conducted to the system from a supply thereof 76 through a valve 93 and line 122 and is generally maintained at a concentration of about 0.1 to about 3% by weight. The mixture of passivated titanium and salt is thereafter fed to a wash system not shown. Various flow meters 81 are positioned throughout the system as required, as are pressure control valves 89 and pressure transducers 86. A filter backwash valve 91 is positioned so that the filter 27 can be backwashed when required if it becomes clogged or otherwise requires backwashing. Standard engineering items such as valves 93, vacuum pump 95 and pressure transducers 86 are situated as required. Symbol 100 is used to denote that parallel systems identical or similar to all or a portion of the system 10 illustrated may be operated simultaneously or in sequence.

In the Armstrong process, the production of the metal, alloy or ceramic is continuous as long as the reactants are fed to the reactor. The present invention provides a separation system, apparatus and method which permits the separation to be either continuous or in sequential batches so rapidly switched by appropriate valving as to be as continuous as required. The object of the invention is to provide a separation apparatus, system and method which allows the reactor(s) 15 in a commercial plant to operate continuously or in economic batches. Reduction of the distillation time in vessel 25 is important in order to operate a plant economically, and economics dictate the exact size, number and configuration of separation

systems and production systems employed. Although described with respect to Ti powder, the invention applies to the separation of any metal, alloy thereof or ceramic produced by the Armstrong process or other industrial processes.

The heating mechanism shown is by fluid heat exchange, but heaters could also be electric or other equivalent means, all of which are incorporated herein. The bottom closure 30 is shown as hinged and is available commercially. The closure 30 may be clamped when shut and hydraulically moved to the open position; however, sliding closures such as gate valves are available and incorporated herein. Although the reactor 20 is shown separate from the vessel 25, the invention includes engineering changes within the skill of the art, such as but not limited to incorporating reactor 20 into vessel 25. Although not shown in Fig. 1, it is contemplated that the slurry as it forms a cake on the filter may be agitated and the cake may be broken to facilitate distillation and/or transfer. Although vessel 35 is illustrated in one embodiment, the vessel 35 could easily be designed as a pipe or the like. Also, the crusher 38 could be located in vessel 25 or intermediate vessel 25 and vessel 35. Moreover, the cake forming on the filter 27 may be broken up prior to or during or subsequent to removal of the liquid metal therefrom. Similarly, when referring to an inert environment, the invention includes a vacuum as well as an inert gas. An important feature of the invention is the separation of vessels 25 and 35 so the environments of each remain separate. That way, no oxygen can contaminate either vessel.

In one specific example, a reactor 15 producing 2 million pounds per year of titanium powder or alloy powder requires two vessels 25, each roughly 14' high and 7' in diameter with appropriate valving, so that the reactor 15 would operate continuously and when one vessel 25 was filled, the slurry product from the reactor would switch automatically to the second

vessel 25. The fill time for each vessel 25 is the same or somewhat longer than the deliquor, distill and evacuation time for vessel 25.

Changing production rates of reactor 15 simply requires engineering calculations for the size and number of vessels 25 and the related equipment and separation systems. The invention as disclosed permits continuous production and separation of metal or ceramic powder, while the specific example disclosed permits continuous separation with two or at most three vessels 25 available for each reactor 15. With multiple reactors 15, the number of vessels 25 and related equipment would probably be between 2 and 3 times the number of reactors.

Referring to Figures 2-4, there is disclosed a system 10A for continuously processing a liquid metal slurry containing particulates. In this description, powder and particulates are used interchangeably. More particularly, the system 10A includes a reactor 11 such as, but not limited to the type shown in the Armstrong Process, including a nozzle 12 through which liquid metal flows and having a housing 14 surrounding the nozzle. A gas inlet 15 serves to introduce gas from a source 16 thereof into the liquid metal thereby producing an exothermic reaction as described in the referenced Armstrong patents. The product from the exothermic reaction may be a slurry of a liquid reducing metal, such as sodium, having dispersed therein particles of the element or alloy produced, such as titanium or an alloy thereof, and the reaction product from the gas, which may be sodium chloride or combination of chloride salts, as in the case of sodium and titanium tetrachloride. The slurry leaves the reactor housing 14 through an outlet 18 and is introduced into a receiving vessel 20 having near the top thereof a dome portion 21 and a cylindrical portion 22 terminating in a frustoconical portion 23 having a discharge outlet 25 at the bottom thereof terminating in a circular flange 26. A motor 30 may be mounted at the top of the vessel 20 connected to an output shaft 31

having an agitator 32 at the bottom of the cylindrical portion 22 or the frustoconical portion 23 as illustrated, for a purpose hereinafter set forth.

Indexing filter system 35, as seen particularly in Fig. 3, is in communication with the vessel 20 and more particularly includes a housing 36, having a top 37, a cylindrical side wall 38 provided with opposed upper apertures 39 and opposed lower apertures 41. The housing 36 is also provided with an outlet 43 having a conduit 44 extending therefrom, for a purpose hereinafter set forth.

An index drive 45 includes a motor 46 having an output shaft 47 in communication with a clutch mechanism 48 connected to an axle 49, the end of which rests in a bearing 51. An aperture 49A is provided in the cylindrical wall 38 to accommodate the axle 49.

An indexing disc 55 is rotatably mounted on the axle 49, the disc having a plurality of longitudinally spaced apart chambers 56 therein, six such chambers being shown for purposes of illustration.

A filter 60, preferably but not necessary a metal wedge wire, is positioned in exit conduit 65 and has a collar 61 maintained in sealing contact with the disc 55 through a spring and pin arrangement 62. The chambers 56 in the disc 55 are also in contact with a collar and spring and pin arrangement in communication with an inlet conduit 63 so as to provide a sealing arrangement for each chamber 56 as it rotates about the axle 49. There is, as illustrated in Fig. 3, a T-shaped conduit 66 having flanges and seals 67 connecting the outlet 25 of the vessel 20 to the indexing disc 55, there being provided a sealing flange 26A (Fig. 2) with the usual seals (not shown) to provide a suitable connection between the vessel 20 and the indexing filter system 35.

Compaction ram assembly 70 is mounted to the housing 36 of the indexing filter system 35 and includes a piston rod 71 having mounted thereon a piston 72. The piston rod

71 is surrounded by a bellows seal 73 and is connected at one end to a suitable drive or motor assembly 74 for longitudinal movement toward and away from the chamber 56, as will hereinafter be described.

A discharge ram assembly 80 is mounted to the housing 36 including a similar piston rod 82, bellows seal 83 and drive motor 84 which is similar to the compaction ram assembly 70. In the illustration of Fig. 3, the discharge ram assembly 80 is rotated for clarity but may be positioned anywhere around the housing 36 in which a chamber 56 is positioned during the indexing of the disc 55, as is well understood by any competent engineer. Moreover, the system 10A of the present invention may also include two or more compaction ram assemblies and two or more discharge ram assemblies, each version being a matter of choice of design, well within the skill of the art. The discharge ram assembly 80 further includes, as did the compaction ram assembly 70, collars 86 and springs and retaining pins 87 to ensure a seal between the discharge ram assembly 80, the indexing disc 55 and the outlet conduit 90 which is surrounded by an outer containment tube or conduit 91, for a purpose hereinafter described.

A cake breaker 93 which may be in the form of a stationary grid or flexible members is positioned at the end of the distillation system 95, as will be explained and for a purpose hereinafter described.

A distillation system 95 is in communication with the outlet conduit 90 of the indexing filter system 35 and includes a longitudinally extending conveyor 96 in a container 98 having a heat exchanger 97 in heat exchange relationship therewith. The distillation system 95 is in communication with a condenser assembly 100 by means of one more tubes 101 extending from the container 98 to a condenser container 103, it being understood that the condenser container 103 is shown for purposes of illustration as an elongated container but

may be of any size or shape as determined. The condenser container 103 is also connected by the conduit 44 to the outlet 43 of the housing 36. A conduit 102 provides communication between the condenser assembly 100 and a liquid metal supply 105 in the form of vessel having connected thereto a distillation vacuum pump 106 and an outlet pipe 107. A pump 108 pumps liquid metal from the supply vessel 105 through a conduit 109 to a liquid metal accumulation tank 115. The tank 115 also receives liquid metal from a head tank 110 in communication with the outlet conduit 65 from the indexing filter system 35, the head tank 110 being in communication with the accumulation tank 115 by means of a conduit 113. A heat exchanger 112 may be in heat exchange relationship with the outlet conduit 65 if heat is needed to be added or removed from the liquid metal exiting the indexing filter system 35, as will be explained.

A vessel 120 is positioned in communication with the distillation system 95 and includes a valve 121, the vessel 120 being in communication with a pump 122 which in turn is in communication with a vessel 125 or lock hopper which is also provided with a valve 126 at the bottom thereof. The vessel or lock hopper 125 through valve 126 is in communication with a passivation system 130 which includes a containment vessel 131, a conveyor 132 in communication with a gas inlet conduit 133 and a gas outlet conduit 134 in communication with a pump 135. The passivation system 130 has an outlet 136, all for a purpose hereinafter set forth.

Operation of the system 10A is as follows. A supply of gas 16 is brought to temperature in a boiler which is meant to be included in the vessel 16 and is transmitted through a conduit or gas inlet pipe 15 into a nozzle 12 through which flows the reductant metal, such as sodium. Sodium is provided from the head tank 110 or supply vessel 105. As is understood, these vessels may be combined into one or may be several, it being within the

skill of the art to design the exact combination of parts in the system. Liquid metal pump 105 provides a continuous flow of liquid metal to the nozzle 12 and the amount of liquid metal and gas is adjusted to maintain the temperature in the reactor 11 at a predetermined but generally low temperature of about 400°C. It is understood that various temperatures may be selected as the operating temperature but about 400°C is preferred at the present time. The reaction products in the reactor 11, as previously explained in the Armstrong et al. patents incorporated herein by reference and the illustrated example herein, comprise a slurry of excess sodium, sodium chloride particles and titanium particles. This slurry flows through outlet conduit 18 into the receiving vessel 20. The temperature of the material at this time is still approximately the outlet temperature from the reactor 11 which may be for instance, about 400°C. In the vessel 20, the slurry is stirred in the vessel when the agitator 32 is operated by virtue of the motor 30. The slurry exits the vessel 20 through the discharge outlet 25 thereof into the indexing filter system 35.

Through gravity, the slurry entering the indexing filter system 35 flows into the T-connector 66 and then into inlet conduit 63 through the filter 60 and into the outlet conduit 65. As the liquid sodium flows through the filter 60 which may be for instance, a 125 micron wedge wire filter, the solids concentration increases as liquid sodium drains. The compaction ram assembly 70 is actuated and the piston 72 drives forwardly into the chamber 56 compressing the material in the conduit 66 thereby expressing liquid metal through the filter 60 until a cake is formed in which most of the liquid metal has been expressed and there remains what could be categorized as wet cake particulate salt and particulate titanium. This cake has sufficient integrity to hold its shape but at the same time still contains some liquid metal. As indicated in the drawing, liquid metal which exits the indexing filter system 35 through the outlet conduit 65 is then recycled to the head tank 110 and moved via the pump

108 back to the nozzle 12 in the reactor 11. After compression by the compaction ram 70 is complete, the motor therefor 74 withdraws the piston 72 and the indexing disc 55 is rotated by the index drive mechanism 45 so as to advance the next chamber 56 into position for another actuation. As is seen from the drawing, because the inlet conduit 66 is connected via gravity to the vessel 20, as soon as the compaction ram 70 withdraws more slurry enters the system. As the disc 55 is rotated as soon as the ram is withdrawn, no slurry material enters the chamber 56 after compaction until the next chamber is in alignment with the compaction ram 70, at which time the aligned chamber 56 fills with the slurry and is thereafter compacted or compressed.

The discharge ram assembly 80 is in alignment or in registry with another chamber 56 of the indexing disc 55 and when the chamber 56 which has the compressed or compacted material therein is in alignment with the discharge ram 80 the piston 82 moves the cake in the chamber 56 into the distillation system 95.

As seen from Fig. 3, there are a plurality of seals 61 and 86 which contain the liquid metal in the appropriate conduit and in its restricted path. However, seals are not necessarily perfect in the real world and although the sealing mechanism in the conduits are intended to provide a seal for the liquid metal, some inevitably may escape and is collected within the housing 36 and flows out of the outlet 43 and conduit 44 into the condenser assembly 100 for further recycle, as will be explained. Although illustrated with one compaction ram assembly 70 and one discharge ram assembly 80, it is well within the skill of the art to include more than one compaction and/or discharge ram assembly 70, 80.

In the distillation system 95, the particulates from the cake are heated by virtue of the heat exchanger 97, which may be via conduction, convection, induction heating or any other suitable commercial method of heating the powder or particulates moved by the conveyor 96

through the cake breaker 93 to the vessel 120. The cake breaker 93 is shown schematically and may be a fixed series of wires or a variety of other mechanical mechanisms which breaks a compacted particulate matter into a loose friable material. Liquid metal which is vaporized in the distillation system 95 is collected and transmitted via conduits 101 into the condenser assembly 100 and container 103 which is maintained at a sufficiently low temperature to condense the liquid metal vapor into a liquid which is transmitted to storage, such as in head tank 110. As previously described, eventually the liquid metal in the tanks 105 and 110 is recirculated via the pump 108 to the reactor 11 and more particularly the nozzle 12. A valve 121 exists between the vessel 120 and the vessel or lock hopper 125. In addition, pump 122 is in communication with the vessel or lock hopper 125 to ensure no vapors back-up into the system 10 and to evacuate the system if it is necessary to isolate the lock hopper 125 by actuation of the valves 121 and 126. From the lock hopper 125 granular material is transmitted to the passivation system 130 and more particularly to a conveyor 132 which moves within a containment vessel 131 while a passivating gas or liquid is provided through the gas or water inlet or conduit 133. As illustrated, the particulates move in countercurrent relation to the passivation material but may not be required to do so. Preferably, the passivation fluid is a gas containing a small percentage such as 0.2% by volume oxygen and an inert gas such as argon. The passivated material then moves through outlet 136 to a wash and dry system 140. A pump 135 and conduit 134 exhaust the passivating fluid and recycle same, if desired.

Referring now to Fig. 5, there is shown an alternate embodiment of the present invention in which like numbers have been applied to like parts. The principal difference in the embodiment of Fig. 5 is that the indexing disc 55 as well as the indexing filter system 35 is arranged horizontally instead of vertically so that as slurry drains from the bottom of the

vessel 20, liquid reducing metal drains through the filter 60 and a compaction occurs after rotation of the indexing disc 55. Thereafter upon further rotation, the discharge ram assembly 80 is actuated to move the cake into the distillation system 95. Other than the positioning of the indexing disc 55, requiring an indexing between recovering slurry and compaction, the operation of the two systems is identical.

On the assumption that a single Armstrong reactor can produce 2,000,000 pounds per year of product, such as titanium or a titanium alloy such as titanium, 6% aluminum and 4% vanadium, the chambers 56 would be 10 inches in diameter and 6 inches in length. Preferably there are 6 such chambers in each disc 55 based calculations that the slurry and/or gel produced in the Armstrong Process which is approximately 22-23% solids by weight. The indexing disc 55 will be indexed approximately every 11 seconds based on the above-described chambers. Different volume chambers or number of chambers will require different indexing times, but this is well within the skill of the art. Under the present example, the material in the chamber 56 will be compressed by a factor of 4 so that the cake ejected by the compaction ram assembly 80 will be about 1.5 inches thick and have a solids composition between about 64 and 65 percent by weight.

Referring now to Fig. 6, there is disclosed a schematic representation of the various processes and products made in accordance with the present invention. The reduction box is the Armstrong Process in which an exothermic reduction occurs controlled by the use of constituents taught in the above-mentioned and incorporated Armstrong et al patents. The separation is as previously described herein along with the passivation. The passivated material then is transmitted to a wash and dry assembly 140 in which the salt product, in this specific example, sodium chloride, is removed from the product particulates, in the example titanium or titanium alloy powder. Referring to Fig. 6, the schematic shows that the powder

may be melted to form an ingot or other solid product by a variety of methods such as casting or transmitted to a powder metallurgy process which includes, but is not limited to, for instance isostatic cold processing, hot isostatic processing using pressure to densify the metal powder into a predetermined shape and density. The product may also be produced by cold spraying the metal powder in a gas jet or subjecting the metal powder to a laser or spheridizing the metal powder by plasma. The metal powder may be formed into a foam and thereafter pressed and sintered to form a stable metal foam as is well known in the art. The powder may be pressed onto a mandrel and thereafter rolled into a thin wall tube. Moreover, powder product may be formed by drawing or extruding the metal powder. In the event that product morphology such as the packing fraction, mean size or size distribution needs to be altered, attriting mechanism may be used to change the morphology of the powder, including the packing fraction or reducing the overall size distribution of the powder.

All these methods of producing product as well as the products formed thereby when combined with the present separation process are included in the present invention.

P-trap is the pressure above the filter (assume downstream pressure remains constant) as the run progressed. Flow 2 is the Na flow rate and the V reactor shows when the product was made. At $t=8420$, sodium flow was initiated to the trap. Trap pressure remained relatively constant as the Na flowed through the clean filter (125 micron) until the reactor valve was opened and started to build cake. The cake DP grew in a linear fashion until $t=8520$ when the reaction rate began to slow because of nozzle plugging due to subsonic operation of the nozzle. The cake thickness after distillation was measured to be on average 5 to 6 inches. The bottom of the cake appeared less dense than the top of the cake and measurements of the cake density showed a density in the top of the cake of 1.1 g/cc and in the bottom of the cake .73 g/cc. It is believed that the bottom was less dense because it was

formed at a lower pressure. For example, the DP is determined by the flow rate; for this run the flow rate was 30 kg/min. Also, after product production was terminated and Na flow continued, the cake appeared to compact further (see pressure increase while flow decreased after $t=8550$). Prior to Na flow shutdown, DP was up to 22 psig versus 18 psig when significant product production ended, see Figs. 1 and 2, see Figs. 7 and 8.

Heat was applied to the cake area and vapor was removed to a primary condenser out the top side of the trap and to a secondary condenser by distilling through the wedge wire filter. During the distillation, a total of 5.9 kg of Na was removed from the cake which weighed 3.4 kg after the distill. 3.8Kg of the 5.9 kg was found to have condensed in the secondary condenser, see Fig. 9.

In another nutsche run, the trap was designed to allow distillation through the filter into the bottom of the trap to utilize the full trap diameter for vapor movement. The trap also had the standard 1" line to a primary condenser, see Fig. 10. Heat was concentrated on the cake area while the bottom of the trap was maintained cool to support condensation of the Na. After distillation, 1.6 kg of Na went to the primary condenser and 1.3 kg. of Na distilled into the bottom of the trap leaving a 3.1 kg. cake of titanium and NaCl.

However, it has been found that breaking the filter cake drastically reduces the distillation times and rates for the distillation of the liquid metal, such as sodium. Using a breaker bar or some other mechanical means such as moving fingers or a mixer has significantly reduced the first portion of the vacuum distill from 40,000 - 50,000 seconds (11-14 hours) to 20,000 to 30,000 (between about 6 and 8 hours). The second portion of the distill, that is the decreasing temperature and pressure portion referred to as the tail was not affected by breaking the filter cake.

It has also been discovered that using a sweep of inert gas such as argon heated, preferably in the range of from about 500°C to about 800°C. during the second distill or tail portion reduced the amount of time necessary to distill the reductant metal (sodium) from about 40,000 - 50,000 seconds to about 10,000 seconds (about 3 hours.). This is a significant improvement over the prior method. By using either one of the methods or a combination of breaking the filter cake combined with an inert gas sweep, the distillation times can be decreased from about (22 or 28) hours to about (9 to 11) hours. This is of significant importance in the design of plants by simplifying designs, reducing collection tanks, valves, piping and other associated equipment.

After vacuum distillation is apparently complete, any remaining trapped reductant metal (sodium) becomes impractical to remove. While it seems obvious to introduce the filter cake into water to wash the residual salt (NaCl) from the titanium powder, the problem exists of trapped reductant metal (sodium) in the filter cake which when combined with water could produce a significant explosion. It is a fact that the mixture of sodium liquid and water will provide an explosion having energy greater than the equivalent amount of TNT.

It has been found in the production of Ti by the subsurface reduction of TiCl_4 by Na that crumbling the filter cake into small quantities, such as less than about five centimeters in diameter and preferably in the range of from about two to about five centimeters in diameter, during or subsequent to the distillation of sodium apparently makes particles or clumps small enough that any trapped Na is manageable without significant damage to equipment or harm to personnel, if proper care is taken in equipment design and with appropriate safety precautions. After distillation, the filter cake is friable and easily crumbled. To the extent that large quantities of crumbled filter cake can be water washed without fear of explosion significantly reduces the distillation times required in the production of the various elemental

material and alloys described in the above-referenced patents, particularly where sodium or other alkaline metal is used as a reductant.

Alternatively, it has been found that the entire distillation can be accomplished at positive pressure, such as, but not limited to, psig with a heated or hot inert gas, such as but not limited to Ar at about 500°C to about 800°C followed by cooling to condense the vaporized liquid metal, such as but not limited to Na. Thereafter, the cooled liquid metal will be returned for additional use.

Summarizing this invention relates to mechanism and methods for decreasing the distillation time of a filter cake produced by the process described in the above-referenced patents. The filter cake can be broken such as by vibration or moving mechanism in the filter cake area or by stationery mechanical bars or members in the filter cake area or other suitable mechanism. An inert sweep gas with or without vacuum can be used alone or in combination with the above described methods breaking the filter cake during the distillation in order significantly to reduce the distillation time of the liquid metal in the filter cake.

Referring to Fig. 11 of the drawings, there is shown a transfer mechanism 10E which includes a double walled conduit including an outer conduit wall 11 having a liquid outlet 12 and end walls 13, the wall 11 being preferably but not necessarily cylindrical. Interior of the cylindrical wall 11 is an inner tube or conduit 15 having a portion 16 which is solid and a portion 17 which is apertured and may be a mesh of any suitable size. The inner tube or conduit 15 may either be cylindrical as illustrated in Fig. 1 or conical as will be explained, the inner conduit 15 has a discharge end 18 thereof which opens into a vacuum chamber 25 and has an inlet end 19 thereof which opens into a container or vessel 20 in communication with the reactor as illustrated in the Armstrong patents previously referenced and incorporated herein.

A feed screw 30 is positioned within the inner conduit 15 and includes a rotatable shank 31 having a conical thread 32 positioned on the shank 31 as is well known in the art. The thread 32 may have a constant or a variable pitch. The pitch is the distance between adjacent threads and the variable pitch may preferably be a progressive pitch in which the pitch decreases from the vessel 20 toward the container or vessel 25, for a purpose hereinafter described.

In the preferred but not limiting embodiment of the present invention, the transfer mechanism 10E is used in conjunction with a material made by the Armstrong Process. More particularly, for purposes of illustration only, the slurry discussed herein will be a combination of liquid sodium, sodium chloride particles and particles of titanium and/or a titanium alloy. As set forth in the Armstrong patents, a variety of metal and non-metal products may be made thereby and it is intended that the present invention not be limited to any particular product made by the Armstrong Process and certainly not limited to the preferred product described herein.

In any event, the vessel or container 20 preferably operated under an inert atmosphere or under vacuum has therein a slurry of the particles previously described and as the slurry enters the portion 19 of the inner conduit or tube 15 and the feed screw 30 is rotated as illustrated in the drawings by rotation of the shank 31, the slurry is moved along the feed screw from left to right as illustrated in Fig. 11. Because of the progressive pitch of the feed screw 30 in Fig. 11, that is the threads 32 thereof are closer together so that the pitch decreases from left to right, the material is concentrated as it is moved from the container or vessel 20 to the container or vessel 25. Moreover, because the portion 17 of the conduit or tube 15 is apertured or porous, liquid sodium drains therethrough and passes out of the outlet 12 for further processing. Therefore, the slurry as it is transported from container or vessel

20 to container or vessel 25 becomes more concentrated as liquid is drained therefrom and the density increases as the pitch between the adjacent threads diminishes.

Another way to express what occurs is that the volume between adjacent threads and the wall of the cylinder or tube 16 diminishes as material is moved by the feed screw 30 from container or vessel 20 to container or vessel 25. By the time the slurry is concentrated and reaches the portion 16, the solid portion 16 of the inner tube or conduit 15, a seal is established between the vessel 25 and the vessel 20 which houses the slurry from the reactor. The formation of a seal by the transfer mechanism 10 is a critical aspect of the present invention because separation of liquid sodium and salt from the desired particles of the ceramic or metal alloy, as described in the Armstrong patents may include distillation in a vacuum chamber or a vessel 25 and the Armstrong reactor itself may be an inerted vessel such as with argon. Accordingly, it is important for a seal to be formed between the two containers or vessels in order to permit continuous operation between the two vessels without the necessity of shutting down one of the vessels during transfer or destroying the protective atmosphere in the vessel 20 or the vacuum in vessel 25.

Referring to Figs. 12 and 13, there are disclosed alternate embodiments of the invention. Again with the principle feature that the volume between adjacent screw threads and the container or housing in which the feed screw is positioned diminishes from vessel 20A to vessel 25A. As seen in Fig. 12, the transfer mechanism 10F has a housing 15A conical in shape and the screw 30 therein may or may not be a progressive pitch screw. The screw threads in the embodiment illustrated in Fig. 12 may not need to be closer together, that is the pitch need not be diminished in order to reduce the volume of the material between adjacent threads and the housing wall as the material is moved from left to right or from vessel 20A to vessel 25A. However, it may be advantageous to use both the conical shaped

inner housing 15A with or without a progressive screw 30A depending on engineering considerations.

Referring to Fig. 13, there is shown another embodiment of the present invention 10G in which the shank 31B of the screw 30B is conical in shape with the larger end of the cone being adjacent the vessel 25B and with the pitch between adjacent threads 32B being constant or diminishing. In either case, the volume of the area between adjacent threads and the inner container 15B diminishes as the material is moved from the vessel 20B to the vessel 25B.

Although the invention has been described with respect to an inerted vessel and a vacuum vessel, the invention includes movement and concentration of material from one container to another without compromising the environment of either container. The containers may be connected pipes or vessels, and the environments may be vacuums, inerted atmospheres or otherwise. Central to the invention is concentration of solids in a slurry to transport solids from one environment to another while forming a seal therebetween so as to isolate the environments from each other.

Referring to Fig. 14, there is shown a separation schematic which is a combination of the above referenced applications illustrating another separation process, system and method relating to but not limited by the Armstrong Process, previously described. As in the earlier described systems, apparatus and methods, there are supplies of halide(s) and reductant metal(s) introduced as previously shown into a reactor to produce by exothermic reaction, in one instance, a slurry of a metal powder, salt particles, and excess reductant metal. The reactor is operated under an inert atmosphere, as taught in the Armstrong Patents, and the slurry produced is transferred to a first vessel, also operated under an inert atmosphere and /or vacuum, as will be explained since the separation process may include portions thereof at either or both positive or negative pressure, that is the first vessel is inerted. It is very

important to prevent oxygen contamination of the first vessel during the processing of the slurry to allow continuous production without shutting down the first vessel and seasoning with liquid metal or otherwise to remove oxygen contamination.

There are a variety of means by which the slurry is treated to remove unwanted constituents, such as salt particles and excess reductant metal. But, all involve moving excess reductant metal as liquid or vapor or both from the first vessel, leaving either a wet or dry cake of either metal powder or a combination of metal powder and salt particles. In order to preserve the integrity of the first vessel, there is a second vessel which may be a tank or a pipe or any container operated under an inert atmosphere and/or vacuum into which the treated slurry(either wet or dry and either metal powder or a combination of metal powder and salt particles) is transferred for further processing and which has some lock or valve or seal or plug mechanism to enable transfer of product from the inerted vessels or containers to a non-inerted environment.

As seen in the drawings as previously described herein, particularly Fig.1, there is shown an apparatus in which the slurry is heated in the first vessel to remove excess liquid metal as both liquid and as vapor. The dried cake is transferred to a second inerted vessel for commutation. Agitation in the first vessel, by mechanical means or otherwise speeds up the distillation process and simultaneously breaks the filter cake when formed, also an added benefit. However, without much change as illustrated in Fig.14, the cake can both be broken and the excess liquid reductant metal removed by an inert hot sweep gas, which if hot enough will vaporize not only the excess liquid reductant metal but also the salt particles, leaving the metal powder to move into the second container(which may be a pipe) to pass through the lock mechanism into an optional passivation station or to be packaged without passivation in an inert environment for shipping. As seen, therefore, the first vessel can be used to treat the slurry by heating to produce either metal powder alone or

in combination with salt particles.

As seen in Figs. 2-6, the first vessel in system 10A can include a sequential indexing separation system in which the first vessel of Fig.14 is a combination of receiving vessel 20 and indexing filter system 35 which produces a sequence of squeezed cakes to a second vessel or distillation system 95, as previously described. The second vessel or container of Fig.14 may be disposed horizontally as the distillation system 95 in system 10A illustrated in Figs. 2-6 and may or may not have a conveyor therein, all depending on engineering considerations within the skill of the art. As seen in Fig. 14, material in the second container, which is now dry, but may be either metal powder alone or a combination of metal powder and salt, is moved one way or another through a lock, as illustrated, or a seal or a valve or any comparable mechanism from the inerted condition of the second container to another environment for additional treatment, which may include passivation followed by water washing or simply packaging in inerted shipping containers, as necessary. The lock mechanism may be the variable pitch screw of Fig. 11 or the variations thereof in Figs. 12 and 13 or any other suitable lock mechanism, such as but not limited to a gate valve.

As seen, therefore, the treatment of the slurry in the first vessel under an inert atmosphere or vacuum or combinations thereof may produce a wet or dry cake of metal powder or a combination of metal powder and salt, depending on the separation conditions chosen. Heaters, either internal or external or both, and/or hot inert sweep gases may be used at either positive or negative pressures or combinations of both positive and negative pressures with either the heaters or sweep gas or both to move material, either excess reductant metal alone or a combination of reductant metal and salt, out of the first vessel. Depending on what is transferred from the first vessel, the second container may employ a hot inert sweep gas or other mechanism to isolate the metal powder from unwanted constituents.

Thereafter, transfer is made to the conveyor, or alternate mechanism, for additional treatment or handling. Passivation with an inert gas having a small amount of oxygen after cooling may be employed, as previously described, followed by a water wash and drying before packaging. Alternately, if both the reductant metal and the salt are removed in the first vessel and/or the second container, the water washing and/or passivation may not be required, resulting perhaps in lower oxygen contamination and/or expense.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WE CLAIM:

1. A method of separating metal powder from a slurry of liquid metal and metal powder and salt, comprising introducing the slurry into a first vessel operated in an inert and/or vacuum environment for separation of liquid metal from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal, transferring the salt and metal powder substantially free of liquid metal to a second vessel operated in an inert environment, and thereafter treating the salt and metal powder to produce passivated metal powder substantially free of salt and liquid metal.
2. The method of claim 1, wherein the inert environment is an argon atmosphere.
3. The method of claim 1, wherein the salt and metal powder are crushed to form clumps having diameters less than about five centimeters prior to passivation.
4. The method of claim 1, wherein the liquid metal is separated from the salt and metal powder in the first vessel both as a liquid and as a vapor.
5. The method of claim 4, wherein the liquid metal vapor from the first vessel is transferred to a condenser operated in an inert environment.
6. The method of claim 4, wherein the liquid metal is an alkali or an alkaline earth metal or mixtures thereof.
7. The method of claim 6, wherein the salt is a halide.
8. The method of claim 7, wherein the metal powder is titanium or a titanium alloy.
9. The method of claim 8, wherein the titanium or titanium alloy is CP 1 to CP 4.
10. The method of claim 9, wherein the metal powder has diameters in the range of from about 0.1 to about 10 microns.
11. The method of claim 1, wherein passivation occurs on a conveyor.

12. The method of claim 11, wherein the metal powder is continuously cooled and passivated.

13. The method of claim 1, wherein the environments of the first and second vessels are protected from contamination by oxygen during the production of metal powder substantially free of salt and liquid metal.

14. A method of separating metal powder from a slurry of liquid metal and metal powder and salt formed by introducing a metal halide vapor subsurface of a liquid metal causing an exothermic reaction producing salt and metal powder with the liquid metal being present in excess of the stoichiometric amount required, comprising introducing the slurry
5 into a first vessel operated in an inert and/or vacuum environment for filtration and vaporization of liquid metal from the metal powder and salt leaving principally salt and metal powder substantially free of liquid metal, transferring the liquid metal vapor to a condenser operated in an inert environment to convert the liquid metal vapor to a liquid to be recycled for production of additional metal powder, transferring the salt and metal powder
10 substantially free of liquid metal to a second vessel operated in an inert environment, and thereafter treating the salt and metal powder to produce passivated metal powder substantially free of salt and liquid metal.

15. The method of claim 14, wherein the slurry is heated in the first vessel by contact with a heat exchanger internal to the first vessel having heat exchange fluid pumped therethrough.

16. The method of claim 14, wherein the liquid metal vapor from the first vessel is cooled by contact with heat exchanger internal to the condenser having a heat exchange fluid pumped therethrough.

17. The method of claim 14, wherein the first vessel is heated by both an internal and an external heat exchanger.

18. The method of claim 14, wherein the slurry is introduced into the interior of a candle filter in the first vessel with liquid metal flowing through the candle filter and out of the first vessel.

19. The method of claim 14, wherein the inert environment for the first and second vessels is an argon atmosphere.

20. The method of claim 19, wherein the condenser is operated in an argon atmosphere.

21. The method of claim 14, wherein the environments of the first and second vessels are protected from contamination by oxygen during the production of metal powder substantially free of salt and liquid metal.

22. A system for separating metal powder from a slurry of liquid metal and metal powder and salt formed by introducing a metal halide vapor subsurface of a liquid metal causing an exothermic reaction producing salt and metal powder with the liquid metal being present in excess of the stoichiometric amount required, comprising a first inerted vessel in communication with a heater and a filter for filtering liquid metal from the slurry and for heating liquid metal to vaporize the liquid metal from the salt and metal powder forming a filter cake of salt and metal powder, an inerted condenser in communication with said first vessel for receiving metal vapor and converting same to liquid metal, a second inerted vessel in valved communication with said first inerted vessel for receiving filter cake therefrom; a crusher in or in communication with said second inerted vessel for crushing the filter cake; a cooling and passivating station for receiving crushed filter cake, and a valve mechanism intermediate said first and second vessel and between said second vessel and said cooling and

passivating station to prevent air from contaminating said first and second vessels during transfer of filter cake from said first vessel to said cooling and passivating station.

23. The system of claim 22, wherein said heater in communication with said first inerted vessel is interior of said vessel.

24. The system of claim 23, wherein said heater interior of said inerted first vessel is in communication with a source of heat exchange fluid which optionally is dedicated to said heater.

25. The system of claim 22, wherein said filter in communication with said first inerted vessel is interior of said vessel.

26. The system of claim 25, wherein said filter is a filter forming an annulus with said first inerted vessel into which liquid metal flows, and further including a conduit in communication with said annulus for transferring liquid metal from said first inerted vessel to an inerted liquid metal reservoir.

27. The system of claim 22, wherein said first and second inerted vessels are inerted with argon.

28. The system of claim 27, wherein said condenser is inerted with argon.

29. The system of claim 28, wherein said inerted condenser is in communication with an argon inerted reservoir for liquid metal formed from condensed metal vapor.

30. The system of claim 22, wherein said condenser is in communication with a source of heat exchange fluid which optionally is dedicated to said condenser.

31. The system of claim 22, wherein said valve intermediate said first and second inerted vessel is hinged to open into said second inerted vessel.

32. The system of claim 22, wherein said first and second vessel are integral.

33. A method of separating metal particulates from a slurry of liquid metal and metal particulates and salt particulates, comprising filtering the slurry to form a cake of metal and salt particulates with some liquid metal, breaking the cake and removing liquid metal from the broken cake, and thereafter separating the metal and salt particulates.

34. The method of claim 33, wherein the liquid metal is removed from the broken cake by vacuum distillation.

35. The method of claim 33, wherein the liquid metal is removed from the broken cake with a hot sweep gas.

36. The method of claim 35, wherein the hot sweep gas is an inert gas.

37. The method of claim 36, wherein the inert gas is argon.

38. The method of claim 36, wherein the hot sweep gas is at positive pressure.

39. The method of claim 37, wherein the hot argon sweep gas is at positive pressure.

40. The method of claim 33, wherein the liquid metal is present in the filter cake up to about ten times the weight of the metal particulates.

41. The method of claim 33, wherein the liquid metal is an alkali metal or an alkaline earth metal or mixtures thereof.

42. The method of claim 33, wherein the liquid metal is Na or Mg.

43. The method of claim 33, wherein the metal particulates are Ti.

44. The method of claim 33, wherein the metal particulates are a Ti alloy.

45. The method of claim 33, wherein the salt particulates are a halide.

46. The method of claim 33, wherein the salt particulates are a chloride.

47. The method of claim 33, wherein the metal particulates are Ti or a Ti alloy and the salt is Na or Mg chloride.

48. The method of claim 47, wherein the liquid metal is Na and the salt particulates are NaCl.

49. The method of claim 33, wherein the cake is broken into pieces having diameters up to about five centimeters.

50. The method of claim 33, wherein the cake is broken into pieces having diameters up to about two centimeters.

51. A method of separating metal particulates from a slurry of liquid metal and metal particulates and salt particulates, comprising filtering the slurry to form a cake of metal and salt particulates with some liquid metal, breaking the cake and removing liquid metal from the broken cake, separating the metal and salt particulates, and
5 sizing the metal particulates before water washing to prevent unacceptable explosions upon contact with water.

52. The method of claim 51, wherein the liquid metal is removed from the broken cake by vacuum distillation or by a hot sweep gas.

53. The method of claim 52, wherein the hot sweep gas is argon.

54. The method of claim 52, wherein the hot sweep gas is at positive pressure.

55. The method of claim 53, wherein the hot argon sweep gas is at positive pressure.

56. The method of claim 52, wherein the liquid metal is Na or Mg and is present in the filter cake up to about ten times the weight of metal particulates.

57. The method of claim 56, wherein the metal particulates are Ti or a Ti alloy.

58. The method of claim 57, wherein the cake is broken into pieces having diameters up to about five centimeters.

59. The method of claim 58, wherein the cake is broken into pieces having diameters up to about two centimeters.

60. A transfer mechanism between a first vessel containing a slurry of liquid and solids and a second vessel under vacuum, comprising a housing in communication with said first and said second vessels, a screw having a plurality of helical threads along a longitudinal shank within said housing for transferring material from said first vessel to said second vessel, the volume between adjacent screw threads and said housing diminishing between
5 said first and said second vessels, whereby slurry entering said housing from said first vessel has the solids therein concentrated as the slurry is transported by said screw toward said second vessel while liquid is expressed from the slurry as the solids are concentrated until the concentrated solids form a plug sealing said second vessel from said first vessel.

61. The transfer mechanism of claim 60, wherein said screw is a variable pitch screw.

62. The transfer mechanism of claim 60, wherein said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

63. The transfer mechanism of claim 60, wherein said housing is generally cylindrical.

64. The transfer mechanism of claim 60, wherein said housing is conical with the smallest end being nearest said second vessel.

65. The transfer mechanism of claim 60, and further including in said transfer mechanism slurry of liquid metal and salt particles and particles of a ceramic or a metal or an alloy.

66. The transfer mechanism of claim 65, wherein said liquid metal is Na or Mg.

67. The transfer mechanism of claim 66, wherein said particles of a ceramic or a metal or an alloy are Ti or an alloy thereof.

68. The transfer mechanism of claim 60, wherein said housing is cylindrical and said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

69. The transfer mechanism of claim 60, wherein said housing is conical with the smallest end being nearest said second vessel and said screw has threads of constant pitch.

70. The transfer mechanism of claim 60, wherein said shank has an increasing diameter toward said second vessel.

71. The transfer mechanism of claim 60, wherein at least a part of said housing in liquid communication with said first vessel has a plurality of apertures therein.

72. The transfer mechanism of claim 60, wherein the plurality of apertures is a mesh.

73. The transfer mechanism of claim 60, and further comprising an outlet in said housing for separating liquid flowing through said apertures from the slurry.

74. A transfer mechanism between a first vessel containing a slurry of liquid alkali or alkaline earth metal or mixtures thereof and metal or alloy or ceramic particles and halide salt particles and a second vessel under vacuum, comprising a housing in communication with said first and said second vessels, a screw having a plurality of helical threads along a longitudinal shank within said housing for transferring material from said first vessel to said second vessel, the volume between adjacent screw threads and said housing diminishing between said first and said second vessels, whereby slurry entering said housing from said first vessel has the particles therein concentrated as the slurry is transported by said screw toward said second vessel while liquid metal is expressed from the slurry as the particles are

10 concentrated until the concentrated particles form a plug sealing said second vessel from said first vessel.

75. The transfer mechanism of claim 74, wherein said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

76. The transfer mechanism of claim 74, wherein said housing is generally cylindrical.

77. The transfer mechanism of claim 74, wherein said housing is conical with the smallest end being nearest said second vessel.

78. The transfer mechanism of claim 74, wherein said housing is cylindrical and said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

79. The transfer mechanism of claim 74, wherein said housing is conical with the smallest end being nearest said second vessel and said screw has threads of constant pitch.

80. The transfer mechanism of claim 79, wherein said shank has an increasing diameter toward said second vessel.

81. The transfer mechanism of claim 74, wherein at least a part of said housing in liquid communication with said first vessel has a plurality of apertures therein.

82. The transfer mechanism of claim 81, wherein the plurality of apertures is a mesh.

83. The transfer mechanism of claim 74, and further comprising an outlet in said housing for separating liquid flowing through said apertures from the slurry.

84. The transfer mechanism of claim 83, and further including a slurry of liquid Na, particles of NaCl and particles of Ti or an alloy thereof.

85. The transfer mechanism of claim 83, wherein a double wall housing is provided wherein the inner wall has a portion thereof apertured and a portion thereof solid and the outer wall has said outlet therein, said screw being positioned within said inner wall.

86. A method of concentrating and transferring a slurry from one container to another while sealing the containers, comprising providing communication between the containers, transporting slurry from one container toward another container while expressing liquid from the slurry thereby increasing the solids concentration thereof until a plug is
5 formed between two containers while solids from the plug are transferred to the another container.

87. The method of claim 86, wherein one container is operated under an inert atmosphere.

88. The method of claim 86, wherein one container is operated under vacuum.

89. The method of claim 86, wherein the slurry contains liquid metal and metal particles.

90. The method of claim 89, wherein the slurry contains liquid alkali or alkaline earth metal.

91. The method of claim 86, wherein slurry contains liquid sodium metal and particles of Ti or an alloy thereof.

1/13

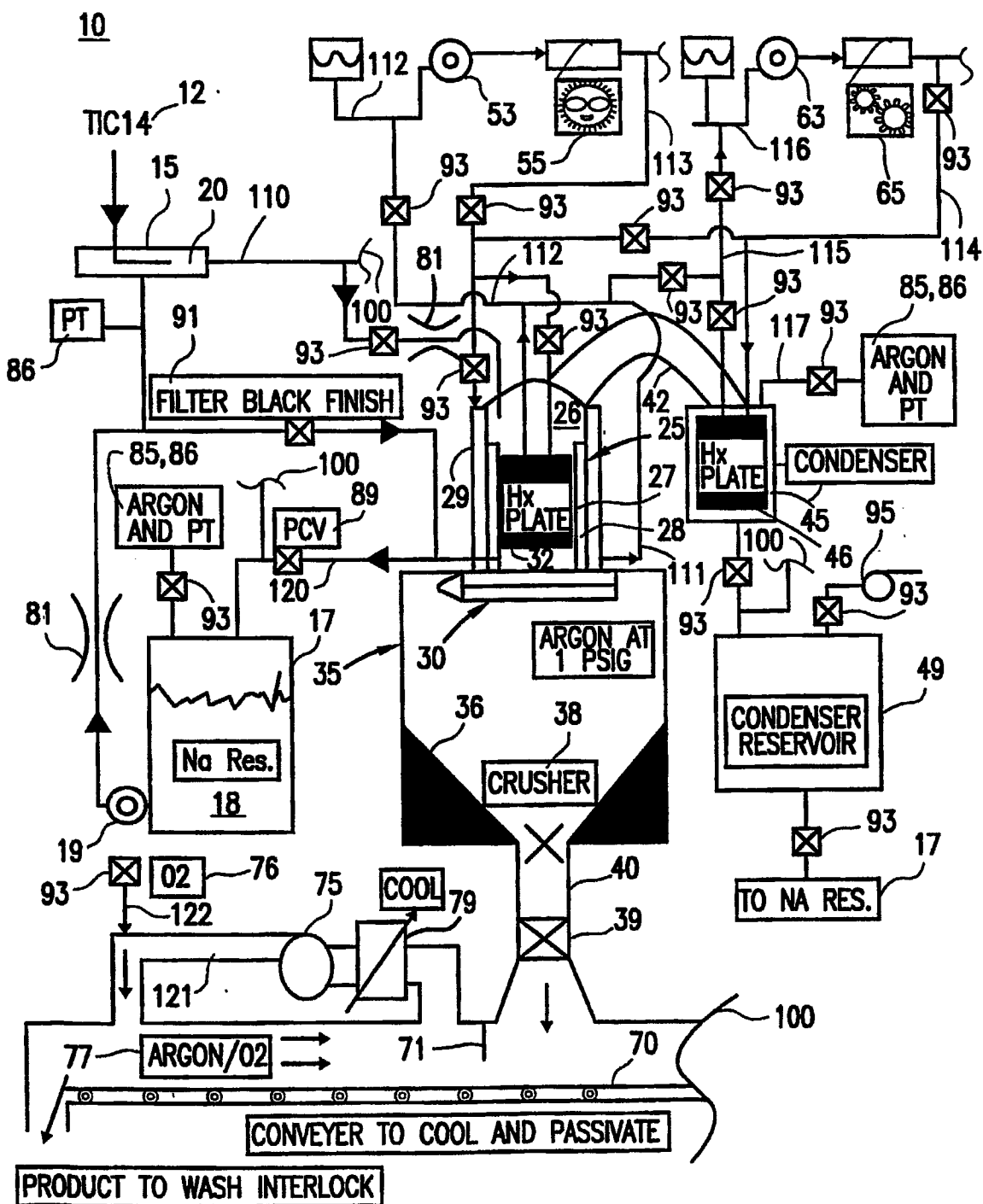


FIG. 1

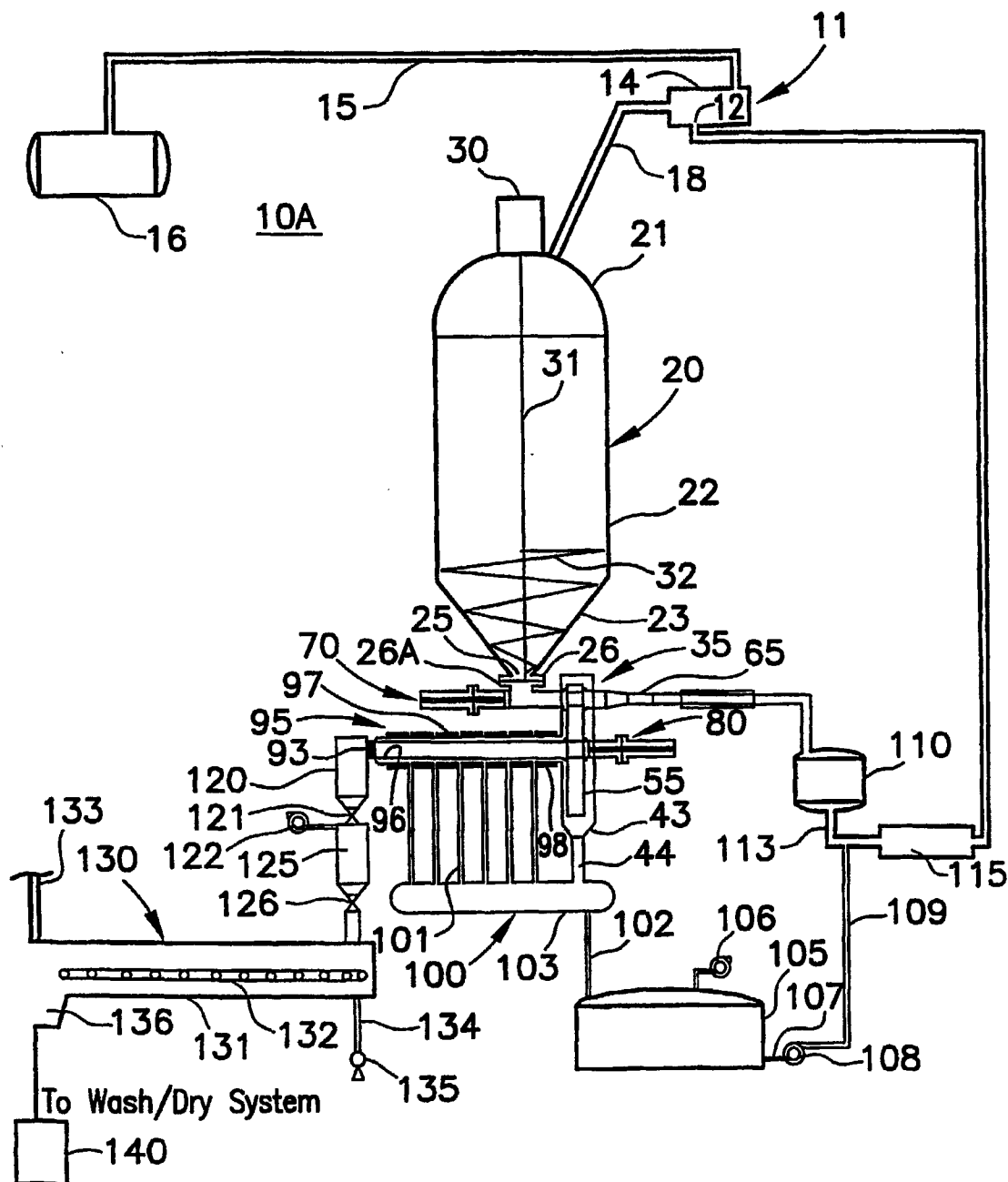


FIG. 2

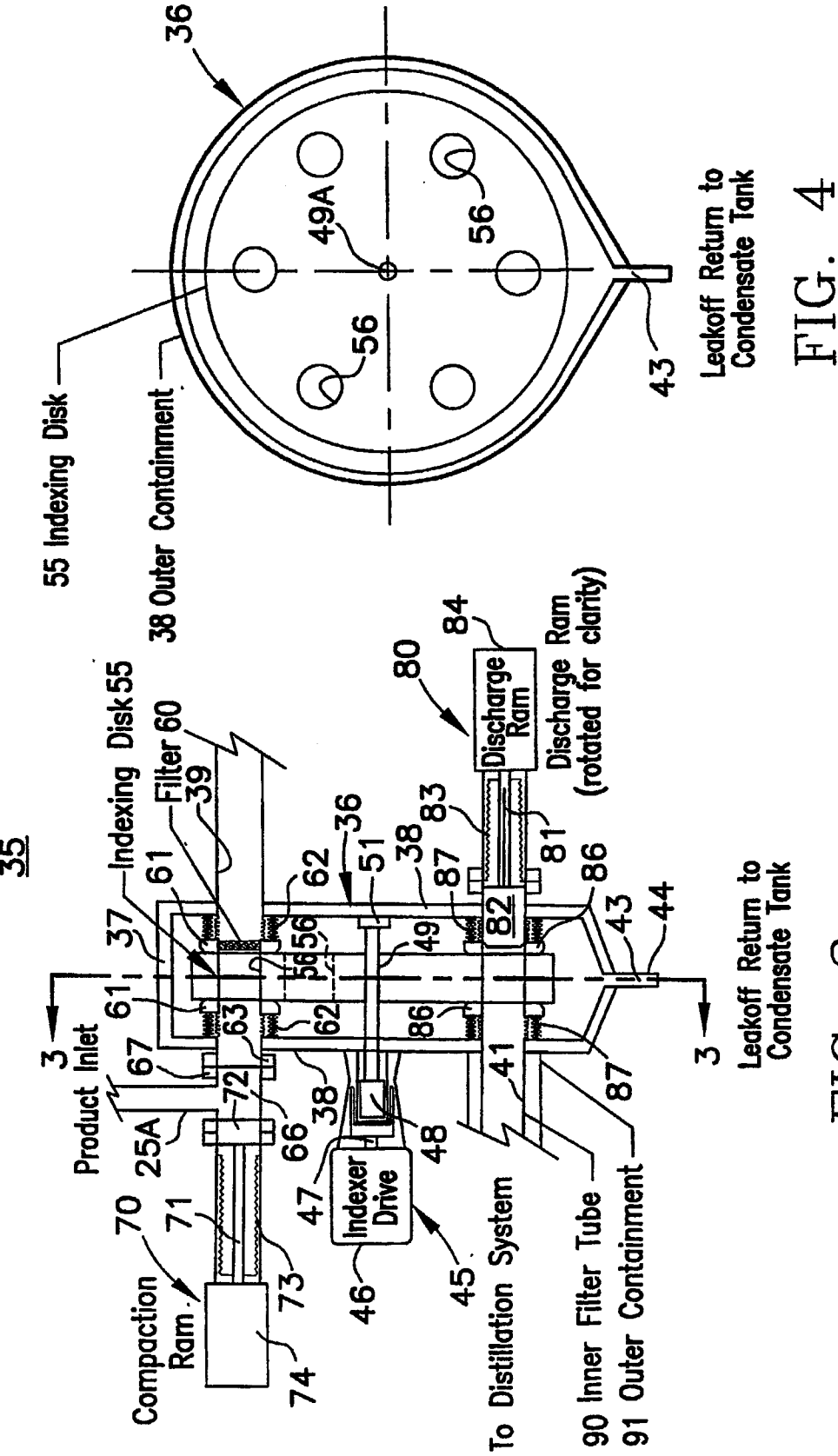


FIG. 3

FIG. 4

4/13

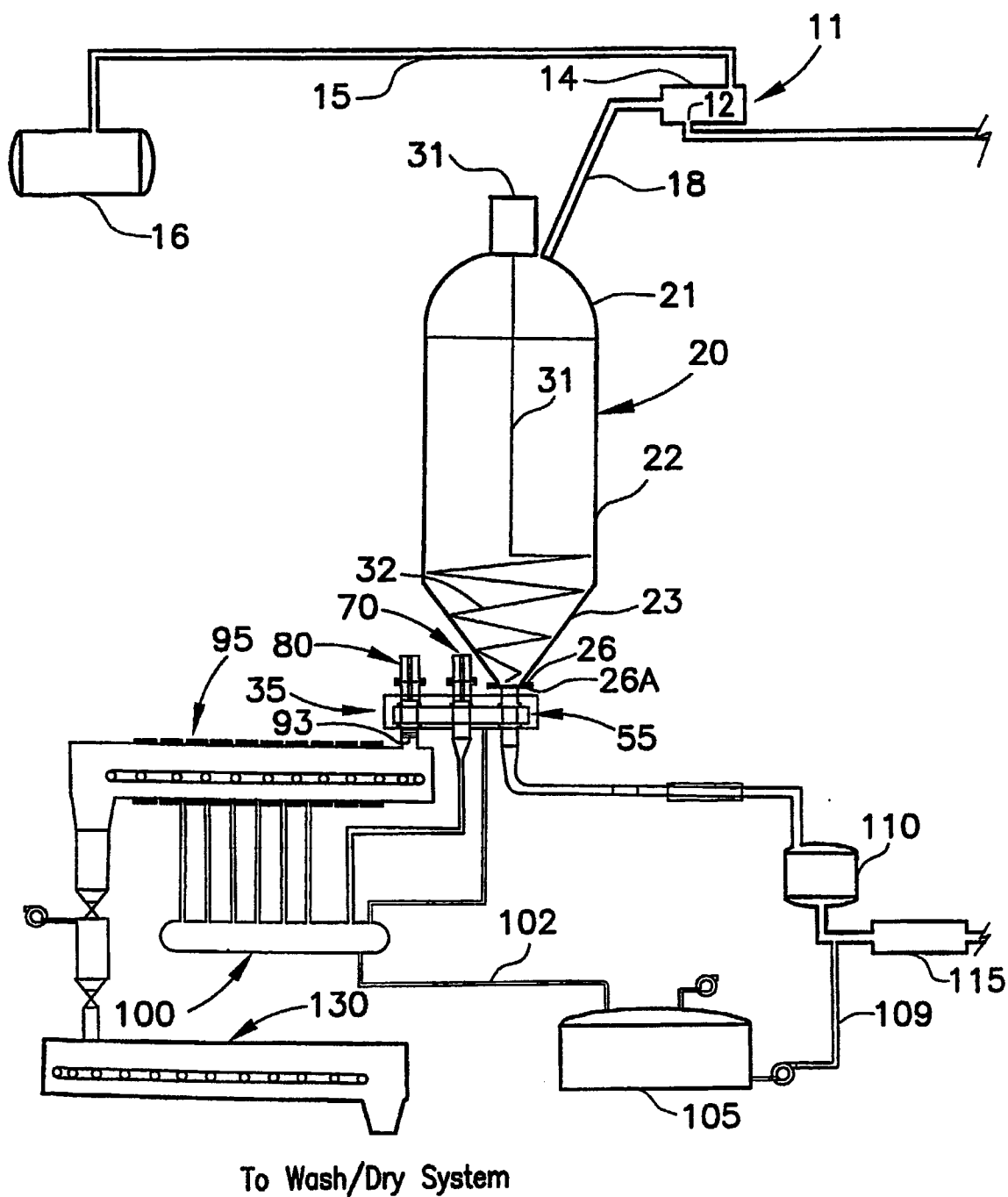


FIG. 5

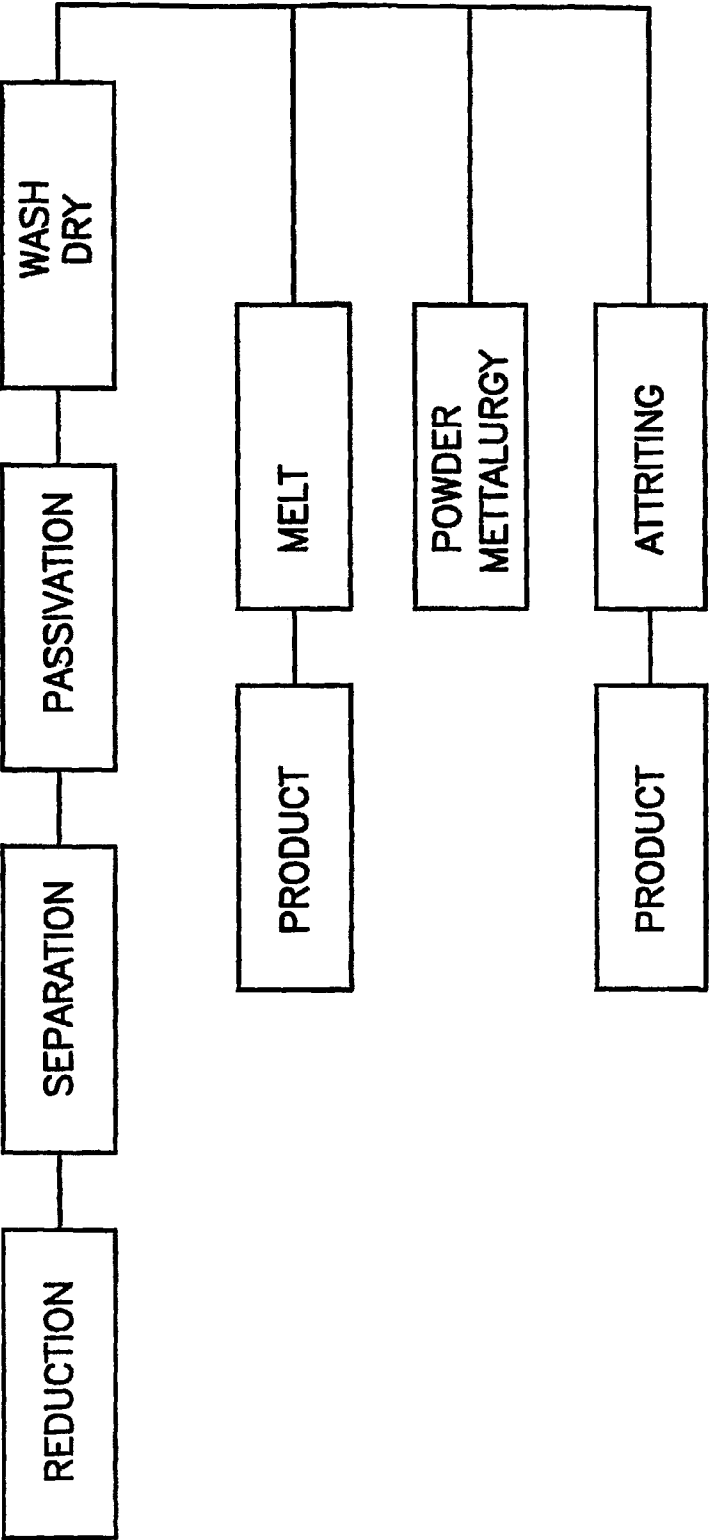


FIG. 6

6/13

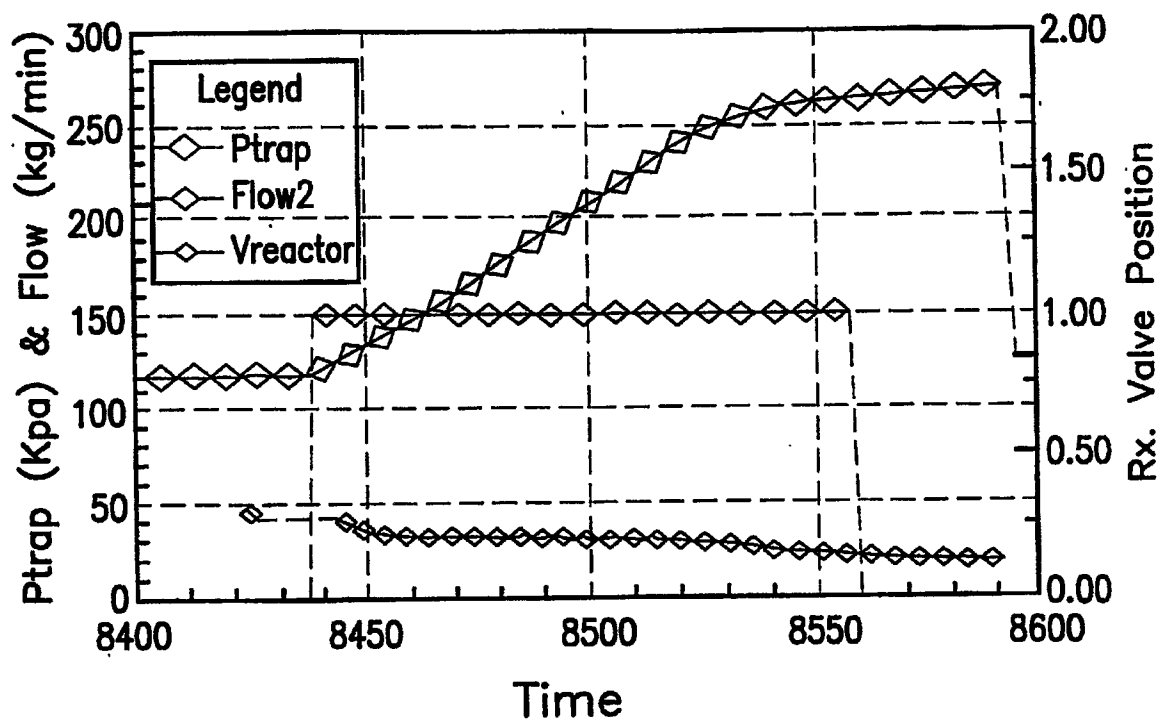


FIG. 7

7/13

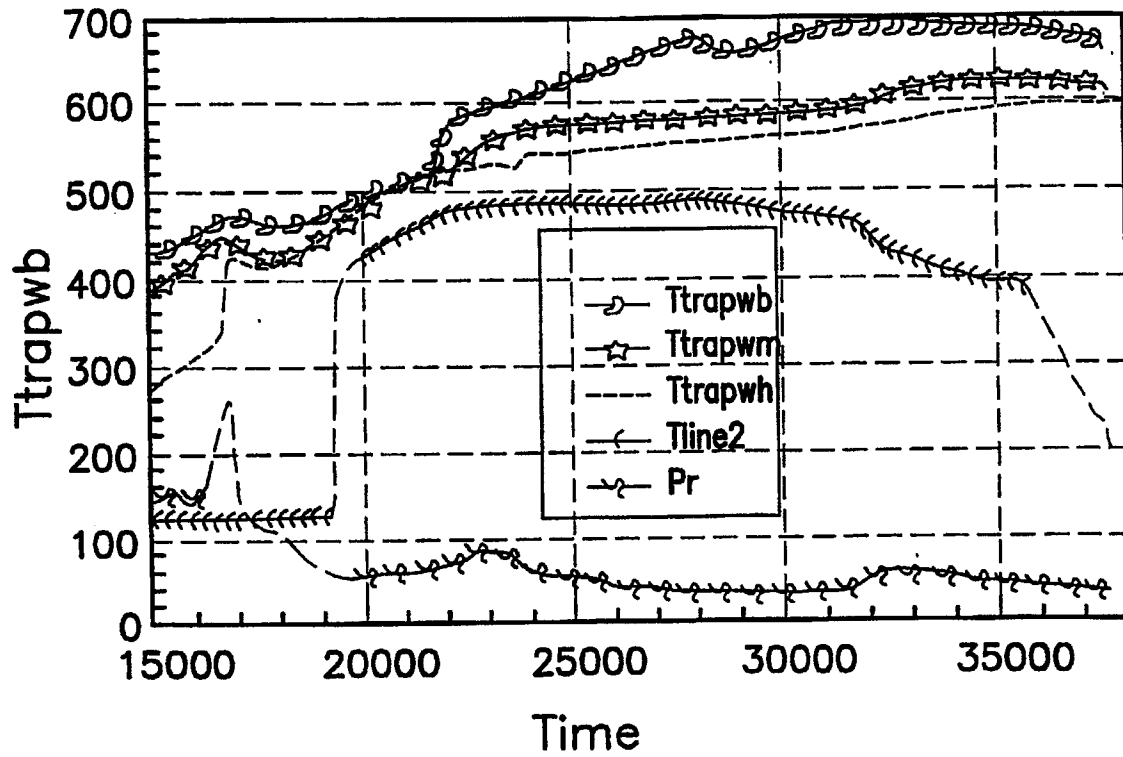


FIG.8

8/13

The distillation setup for this trap was as follows:

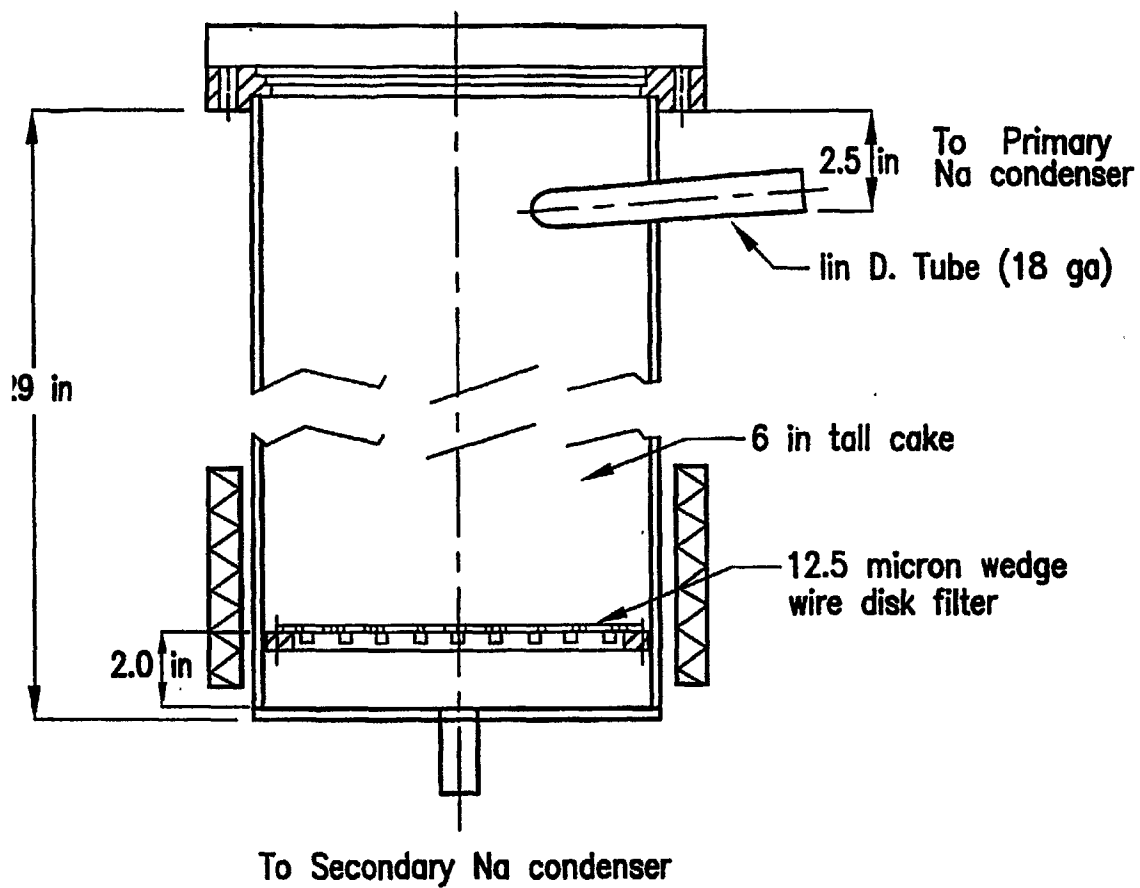


FIG. 9

9/13

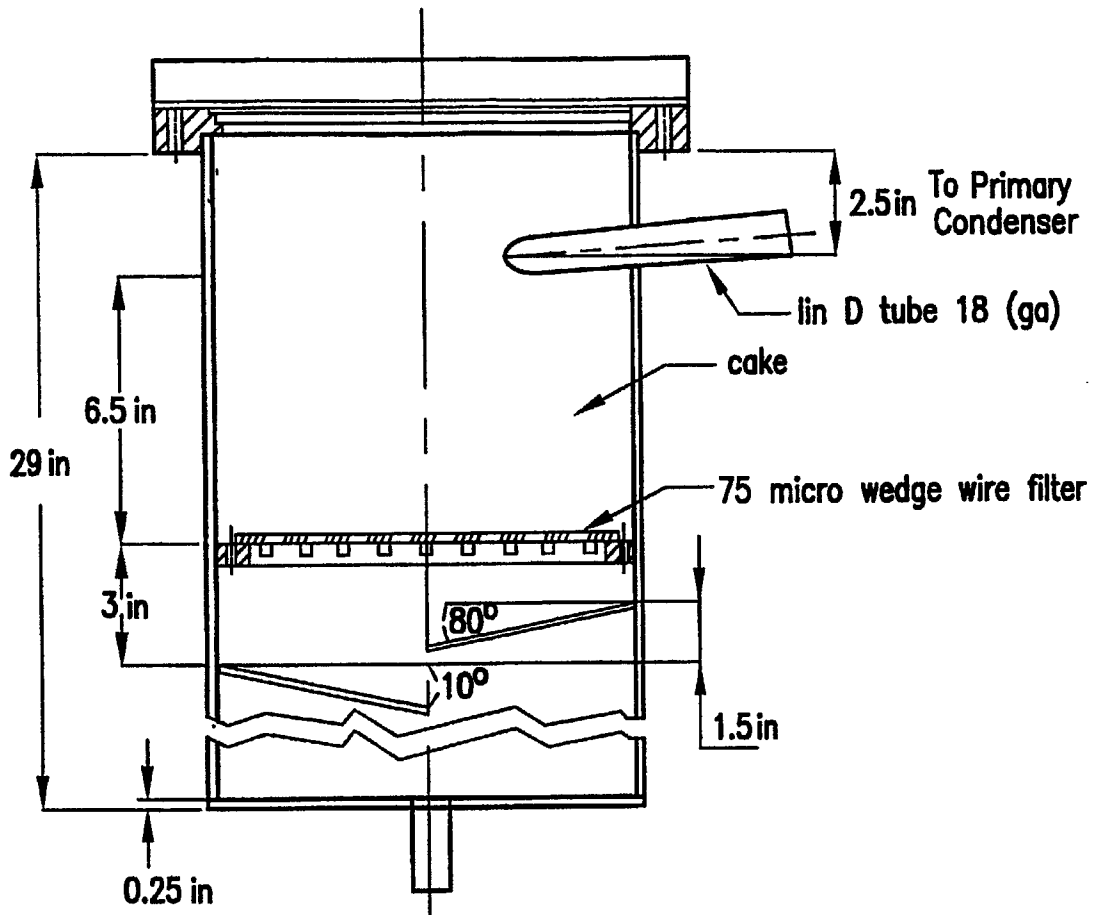


FIG.10

10/13

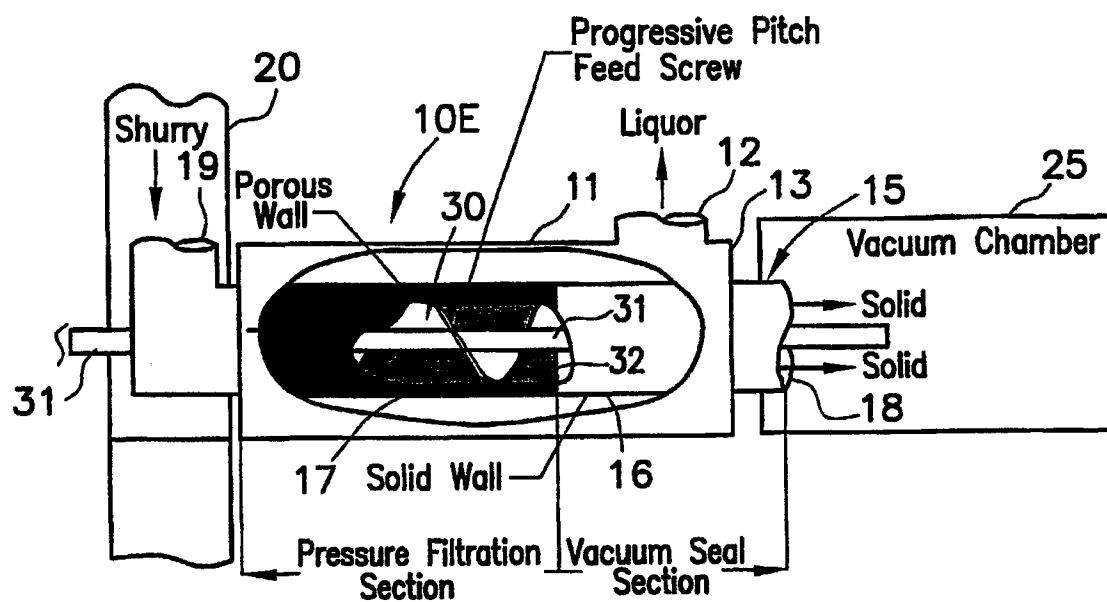


FIG.11

11/13

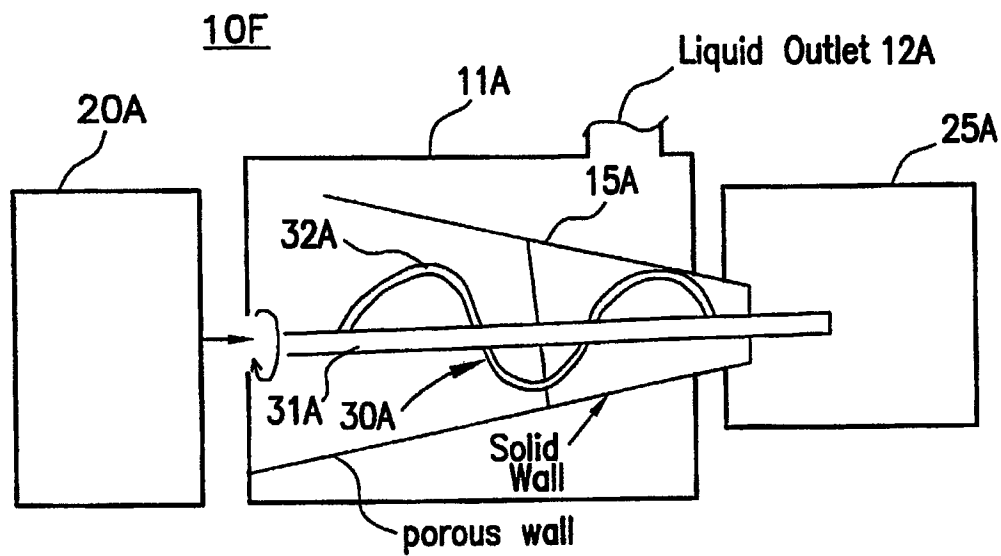


FIG. 12

12/13

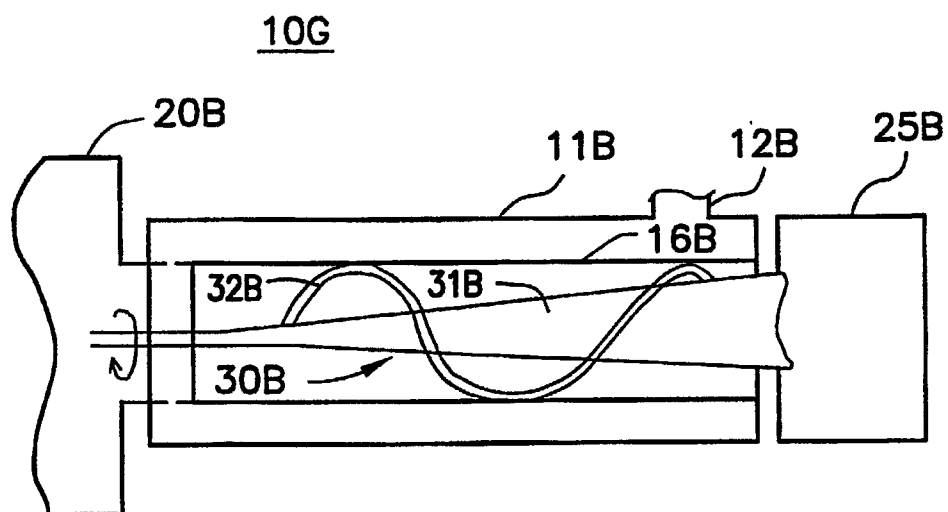


FIG.13

13/13

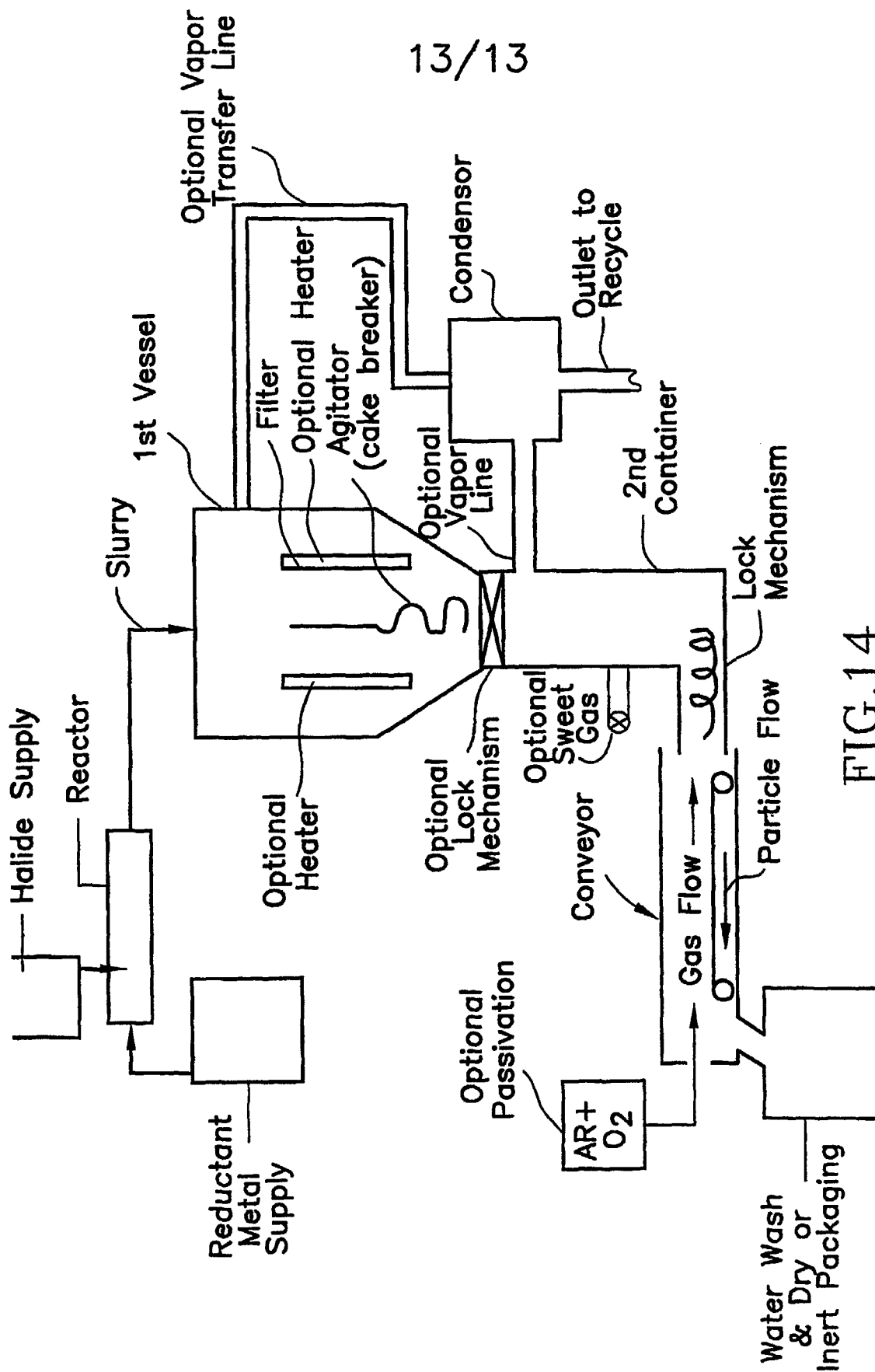


FIG.14

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 March 2005 (17.03.2005)

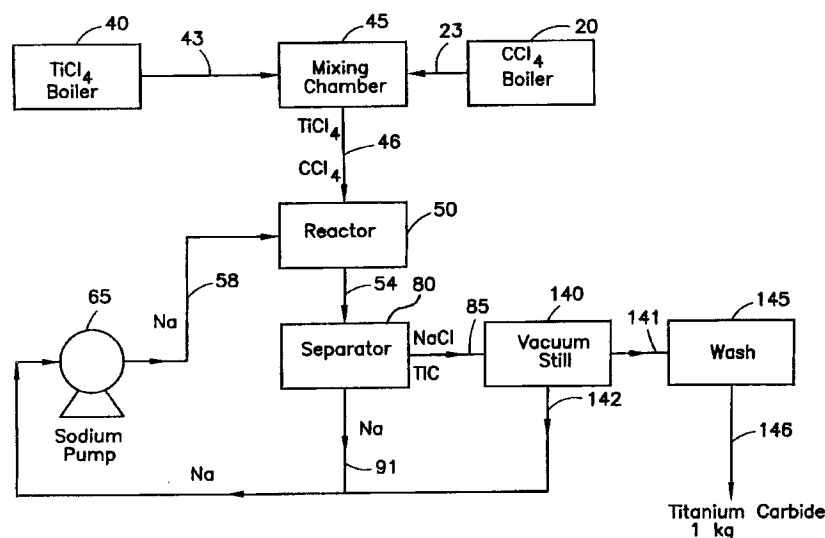
PCT

(10) International Publication Number
WO 2005/023725 A2

- (51) International Patent Classification⁷: **C04B 35/00** (72) Inventors; and
(75) Inventors/Applicants (for US only): **ARMSTRONG, Donn, Reynolds** [US/US]; 6005 Ridge Court, Lisle, IL 60532 (US). **ANDERSON, Richard, P.** [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60514 (US). **BORYS, Stanley, S.** [US/US]; 372 Walnut, Elmhurst, IL (US).
- (21) International Application Number:
PCT/US2004/028528
- (22) International Filing Date:
2 September 2004 (02.09.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
10/654,464 3 September 2003 (03.09.2003) US
- (63) Related by continuation (CON) or continuation-in-part (CIP) to earlier applications:
US 10/238,297 (CON)
Filed on 10 September 2002 (10.09.2002)
US 10/238,791 (CON)
Filed on 10 September 2002 (10.09.2002)
- (71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC** [US/US]; 20634 W. Gaskin Drive, Lockport, IL 60441 (US).
- (74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar LLC, 125 South Wacker Drive, Suite 2080, Chicago, IL 60606 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US (patent), UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: CERAMICS AND METHODS OF PRODUCING CERAMICS



(57) Abstract: A method of continuously producing a non-oxide ceramic formed of a metal constituent and a non-metal constituent. A salt of the metal constituent and a compound of the non-metal constituent and a compound of the non-metal constituent are introduced into a liquid alkali metal or a liquid alkaline earth metal or mixtures to react the constituents substantially submerged in the liquid metal to form ceramic particles. The liquid metal is present in excess of the stoichiometric amount necessary to convert the constituents into ceramic particles to absorb the heat of reaction to maintain the temperature of the ceramic particles below the sintering temperature. Ceramic particles made by the method are part of the invention.



European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv)) for US only

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

CERAMICS AND METHOD OF PRODUCING CERAMICS

RELATED APPLICATIONS

This is a continuation of application Serial No. 10/238,297 and application Serial No. 10/238,791 filed September 10, 2002 which was a continuation of application Serial No. 10/125,988 filed April 20, 2002 and application Serial No. 10/125,942 filed April 19, 2002, which were continuations of application Serial No. 09/264,577 filed March 8, 1999 which was a continuation-in-part of application Serial No. 08/782,816, filed January 13, 1997, Patent No. 5,958,106, which was a continuation-in-part of application no. 08/691,423, August 19, 1996, Patent No. 5,779,761, which was a continuation of application no. 08/283,358, August 1, 1994, abandoned, the entire disclosures of which are incorporated by reference.

BACKGROUND OF THE INVENTION

This invention relates to the direct production of non-oxide ceramic powders of carbides, nitrides, silicides, sulfides, borides or mixtures thereof from volatile compounds in a liquid metal reactor. Particular interest exists for liquid sodium as the reacting metal and the present invention will be described with particular reference to sodium but is applicable to other alkali and alkaline earth metal reducing media. Elemental materials have been successfully made by the Armstrong Process described in U.S. Patent Nos. 5,779,761, 5,958,106 and 6,409,797, but those patents describe the use of one or more halide feed streams, whereas the present invention is related to ceramics using different feed streams than previously disclosed. For the purposes of this invention the feedstocks include those metals that have volatile liquid compounds such as, by way of example only, the halides of

titanium, tantalum, zirconium, aluminum, vanadium and silicon.

SUMMARY OF THE INVENTION

The proposed process is an innovative low-temperature approach to producing non-oxide ceramic powders. The process uses the reaction of liquid metal sodium (or other alkali or alkaline earth metal) and two or more inorganic feedstocks, mixed together and introduced through a sonic nozzle submerged in the liquid sodium, to produce sodium salts of the anions of the feedstocks and the ceramic compound of the cationic constituents of the inorganic reactants. By way of example, a representative reaction to make titanium carbide is as follows:



The reaction products, TiC and NaCl are both solids in the temperature ranges at which the process operates and can be separated from liquid sodium by standard techniques leaving a water soluble salt and a ceramic powder. A mixed ceramic such as TiC/TiN can be made by introducing both carbon and nitrogen compounds into the sodium along with the volatile titanium compound. This may be accomplished by either a mixture of, for example, CCl₄ and N₂ or the single compound C₂N₂ as follows:



Using N₂ permits different ratios of the ceramics to be produced, while using C₂N₂ results in equal molar quantities of each ceramic.

Accordingly, an object of the present invention is to provide a low-temperature and continuous ceramic production process, with short residence times, eliminating the excessive energy consumption requirements of current production technology, while providing great latitude in the product produced.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic representation of a continuous process for carrying out the invention;

FIG. 2 is a representation of a sonic nozzle and reactor for carrying out the invention; and

FIG. 3 is a flow diagram of a process for carrying out the invention.

DETAILED DESCRIPTION OF THE INVENTION

The liquid metal serves both as a reactant and a heat transfer medium. A quantity of each of the inorganic feeds is boiled in one or more inorganic supply tanks at a pressure greater than that required for sonic flow through the submerged injection nozzle. The mixed inorganic vapors flow through the nozzle beneath the liquid metal surface and react with the liquid metal to produce salts of the anionic parts of the feedstocks and ceramic powder. Other methods of obtaining predetermined vapor mixtures are intended to be included in this invention, the

mixing chambers described above being only one.

The process begins with the injection of a vapor mixture through a sonic flow nozzle. Key to the process is the submerged reaction of the inorganic vapor in a liquid metal. The reaction process is controlled through the use of a choked-flow (sonic, or critical-flow) nozzle, described at page 5-14, of Perry's Chemical Engineers' Handbook, sixth edition, McGraw-Hill Book Company, 1984, which is incorporated herein by reference. A choke-flow nozzle is a vapor injection nozzle that achieves sonic velocity of the vapor at the nozzle throat. Then, any change in downstream conditions that causes a pressure change cannot propagate upstream to affect the discharge. The downstream pressure may then be reduced indefinitely without increasing or decreasing the discharge. Under choke-flow conditions, only the upstream conditions need to be controlled to control the flow rate. The choke-flow nozzle serves two purposes: (1) it isolates the vapor generator from the liquid metal system, precluding the possibility of liquid metal backing up into the inorganic feed system and causing potentially dangerous contact with the liquid inorganic feedstock, and (2) it delivers the vapor at a fixed rate, independent of temperature and pressure fluctuations in the reaction zone, allowing easy and absolute control of the reaction kinetics.

The liquid metal stream also has multiple functional uses: (1) it rapidly chills the reaction products, forming solid powder products (2) it transports the chilled reaction products to a separator, and (3) it serves as a heat transfer medium allowing control of the reaction temperature. A liquid metal flow rate is selected to control the temperature increase through the reactor, preferably at less than about 200°C to about 600°C. Liquid metal containing the reaction products, for instance,

sodium chloride and titanium carbide, exits the reactor and enters a separator where most of the liquid metal is removed and recycled to the reactor.

The process of the invention may be practiced with the use of any alkali metal including mixtures thereof, or alkaline earth metal including mixtures thereof depending on the feed stock to be reduced. By way of example, sodium will be chosen, not for purposes of limitation but merely for purposes of illustration, because it is cheapest and preferred. Titanium tetrachloride will be chosen by way of example as one of the reacting inorganic materials and carbon tetrachloride as the other as they are readily available. Other gases useful in the invention include the halides of Ta, Zr, Si, and Al, as well as gaseous compounds of C, B, N, and Si. Mixtures of the gases can be used to manufacture mixed ceramics, such as, by way of example TiC/TiN. Si appears as both a metal constituent and a non-metal constituent, since Si can form ceramics with metals or non-metals.

Referring to Figure 1 there is shown a schematic block diagram representation of the invention in which a carbon tetrachloride boiler 20 is connected via line 23 to a mixing chamber 45. The mixing chamber 45 receives titanium tetrachloride from a boiler 40 through a line 43. In the mixing chamber 45, an apparatus such as a fan (not shown) mixes the two gases which then exit the mixing chamber through a line 46 and enter a reactor 50. The mixing chamber 45 may not require a fan or other means for obtaining a predetermined ratio of gases may be used. In the reactor 50 there is present liquid sodium which enters the reactor through a line 58 and a sonic nozzle 70, see Fig. 2, hereinafter described, which introduces the mixed vapor of titanium tetrachloride and carbon tetrachloride submerged in a liquid sodium environment.

The reaction is exothermic and produces ceramic titanium carbide powder. All products leave the reactor 50 through an exit or outlet line 54. The reacted materials, along with unreacted and excess liquid sodium, enter a separator 80 such as a filter to separate the solids including the reaction products of titanium carbide and sodium chloride from liquid sodium, the liquid sodium leaving the separator 80 via a line 91 and the solids leaving the separator 80 through a line 85 which leads to a vacuum still 140. The vacuum still 140 draws off any entrained liquid sodium and recycles it via line 142 to a sodium pump 65 while the product or combined solids of sodium chloride and titanium carbide are transferred via line 141 to a wash station 145. The product is washed with water thereby dissolving the sodium chloride leaving behind the ceramic titanium carbide powder to exit through a line 146 as product. The wash water containing the dissolved sodium chloride can be disposed of as required.

Referring to Figure 3 there is shown a more detailed engineering diagram in which a carbon tetrachloride supply 10 is connected via line 11 to a metering pump 15 and to the carbon tetrachloride boiler 20. The carbon tetrachloride boiler 20 is fundamentally a heat exchanger 22 operated at a sufficient temperature to flash carbon tetrachloride from a liquid to a gas. A line 23 transports the gaseous carbon tetrachloride from the heat exchanger or flash boiler 20 to the mixing chamber 45. Similarly, a titanium tetrachloride supply 30 is connected via line 31 to a metering pump 35 which transports the liquid titanium tetrachloride to a flash boiler 40 which is also a heat exchanger 42 operating at a temperature sufficient to convert the liquid titanium tetrachloride to vapor. The gaseous titanium tetrachloride is conducted via line 43 to the mixing chamber 45, previously described, for mixing the gaseous

carbon tetrachloride and the gaseous titanium tetrachloride therein, the combined gases leaving through the line 46 and being transported through a valve 47 to the reaction chamber 50.

The reaction chamber 50 consists of a conduit 51 having a sodium inlet 52 and an outlet 53. As shown in the Figure, a sonic nozzle 70 receives the mixed gas from the line 46 leaving the mixing chamber 45 and introduces the gas into the reaction chamber 50, at conditions hereinafter to be described.

Sodium is provided from a source thereof 55, illustrated as a sodium fill sump having an exit line 56 which passes through a valve 57 and becomes line 58 passing through a sodium flow meter 60 and then through a sodium pump 65 into the reaction chamber 50. In the reaction chamber 50, as shown in more detail in Fig. 2, there is a reaction zone 72 wherein the mixed gases from the sonic nozzle 70 (and mixing chamber 45) enter the liquid sodium environment which acts as a heat sink 75. Downstream from the reaction zone 72 is a quench zone 74 denoted in broken lines. It is in the area of the reaction zone 72 that the reaction is believed to take place in the gaseous state, that is the reduction of the mixed titanium tetrachloride and carbon tetrachloride gases to the ceramic titanium carbide occurs at a very elevated temperature due to the exothermic nature of the reaction. The presence of greater than stoichiometric quantities of sodium necessary to reduce the gases to the corresponding elemental material provides a sufficient heat sink 75 and quench zone 74 such that the reaction products are quickly cooled below the sintering temperature of the titanium carbide formed and below the melting temperature of the sodium chloride formed during reaction. The rapid cooling of the reaction products below the melting point of the salt and the sintering temperature of the ceramic are

important features of the present invention.

Another important feature of the present invention is that the entire system can be operated at relatively low temperatures, depending on the reducing metal employed. It is only required that the temperature of the system be greater than the melting point of the reducing metal. In the case of sodium, the system operating temperature must be greater than about 97°C, which is the approximate melting temperature of sodium. For safety sake, of course, the system will be operated at a sufficiently greater temperature than 97°C to accommodate usual engineering fluctuations which occur in operating any system, preferably about 400°C.

Very high temperatures are not needed and are preferably avoided. This low temperature operation is also made possible by the fact that the mixed gases entering subsurface to a liquid sodium environment react completely and are reduced at the relatively low temperatures of the inventive system. In prior art systems, the constituents have to be heated to a much higher temperature to initiate a reaction, but for some reason, introducing the titanium tetrachloride and carbon tetrachloride vapor in a completely liquid sodium environment initiates the reaction at lower than expected temperatures providing all the advantages previously described.

After the reaction occurs, the reaction products are titanium carbide which is a solid particulate material at the temperatures at which the system is operated and sodium chloride which is also a particulate solid at the temperature at which the system operates and unreacted liquid sodium present in greater than stoichiometric quantities. This mixture of material leaves the reaction chamber 50 via a line 54 and is transported to a solids separator 80. The solids separator 80 has a housing 81 and contains a series of baffles 82 which permit the solids to settle out while the

liquid sodium is transported to a pair of filters 90a, 90b. The solids exit the separator 80 through a line 85, and may be transferred to a wash station 145 as previously described. The sodium in the normal operation of the loop exits the solids separator 80 through the filter 90a via line 91 and passes through a heat exchanger 95 wherein heat is removed. As before mentioned the reaction to produce the titanium carbide is exothermic thereby adding a significant quantity of heat to the liquid sodium. It is at the heat exchanger 95 that some of this heat is removed. The cooled sodium exiting the heat exchanger 95 through line 91 passes through valves 97 and 99 and joins with the line 56 to be recycled through line 58 to the sodium flow meter 60 and the pump 65.

A cold trap 100 is provided with a housing 101 and a heat exchanger 102. The cold trap 100 is operated intermittently and is used to precipitate any oxygen which may find its way into the sodium since sodium oxide is a corrosive and unwanted material. The heat exchanger 102 is operated at parameters sufficient to reduce the temperature of the liquid sodium to the point where sodium oxide precipitates. The cold trap 100 has a valve 104 intermediate line 91 and the cold trap inlet 105. A valve 107 intermediate cold trap outlet 106 and line 91 isolates the cold trap 100 from the normal recycle of sodium through the reactor 50 and the solids separator 80.

The filter 90(b) in the solids separator 80 is used only intermittently and when the system is to be drained. The filter has an outlet line 111 leading to a valve 112. Line 111 joins line 109 between a valve 108 and inlet 116 of a drain sump 115. The drain sump 115 is used, as is obvious to those of ordinary skill in the art, to drain the system for clean-up and maintenance. A vacuum pump 120 is connected through

line 118 and valves 122 to drain sump 115, thereby providing the necessary vacuum to the system. The vacuum 120 is also connected through valves 123, 134 and 137 to a line 131 connecting a source of inert gas 130 such as helium or argon and the fill sump 55. Line 131 passes through a flow meter 132. A valve 133 in line 136 connects line 131 with line 118 exiting from the drain sump 115. Accordingly, the fill sump 55 which stores make-up sodium for the system is under an inert gas atmosphere maintained at a pressure determined by the vacuum pump 120.

The operation of the system has been described in general but the reactor 50 may be a 10 cm stainless steel vessel while the heat exchanger 22 and 42 may be constructed of materials and of a design known to persons of ordinary skill in the art. The mixed gas which flows from the mixer 45 into the reactor 50 by means of the sonic nozzle 70 flows at a pressure which is controlled by the boiler temperatures heating the feeds until the vapor pressures of the inorganic feeds exceed the critical pressure ratio as determined by the ambient pressure of the reactor 50. The ambient pressure of the reactor 50 is determined by the vacuum pump 120. The nozzle 70 may have (by way of example only) a diameter of 1 cm and positioned within a 5 cm diameter reaction vessel) 50 so that the gas is completely submerged within the liquid sodium medium. All parts of the apparatus in contact with the inorganic vapors from boilers 20 and 40 must be maintained above the temperature which gives a vapor pressure of both inorganic feeds greater than the critical pressure ratio by suitable heat tracing of the various connecting pipes and control valves, all as is well known in the engineering art. It is imperative, for safety purposes, that the mixed gas flowing through the nozzle 70 into the liquid sodium environment is at greater than sonic velocity.

Accordingly, it is preferred that the vapor be between two atmospheres and about ten atmospheres of pressure in order to ensure that the velocity of the mixed gas is greater than the sonic velocity. By operating at greater than sonic velocity, it is ensured that the sodium does not back up into the nozzle 70 thereby possibly clogging the nozzle but also possibly creating a dangerous environment in which an explosion could occur.

Preferably the sodium is maintained at less than about 600°C. It is understood that because of the exothermic nature of the reaction, that the reaction zone 72 and portions of the quench zone 74 will be at temperatures greater than the operating temperatures of the system. Nevertheless, because of the excess of liquid sodium (or other reducing metal) with respect to the stoichiometric quantities necessary to reduce the titanium tetrachloride and carbon tetrachloride, the quenching action is so rapid that the formed titanium carbide particles do not sinter. This is not to say that the formed titanium carbide particles do not at some instant in time have a temperature greater than the sintering temperature, that is particles may be formed at a temperature in excess of the titanium carbide sintering temperature but they are rapidly quenched to a temperature below the sintering temperature while at the same time being transported downstream due to the flow of sodium past the nozzle 70. It is the combination of this excess of sodium having a high heat capacity along with the flow and mixing generated by the reaction which prevents the titanium carbide particles from sintering to any significant degree which is a major aspect of the present invention. The reaction zone 72 and the quench zone 74 are shown for purposes of illustration only and do not represent an accurate determination of how far downstream the zones extend.

Although the example given refers to titanium carbide as the product, it should be understood that a variety of ceramics can be made by the subject invention. Most preferably, volatile liquid compounds such as the halides of titanium, tantalum, zirconium, silicon and aluminum may be combined with one or more of various halides of carbon, boron, silicon, sulfur and/or various other gaseous compounds, such as C_2N_2 or others in order to provide single or mixed ceramics. As before stated, mixed compounds such as cyanogen (C_2N_2) may be used as a feedstock alone or in combination with other sources of non-metallics to provide mixed carbide and nitride ceramics, while other non-metal constituents, such as boron, silicon and sulfur, may be used to provide a variety of ceramics. In separating the produced salt, distillation is probably preferred to water washing, but this is within the skill of the relevant art.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WE CLAIM:

1. A method of producing a ceramic formed of a metal constituent and a non-metal constituent from a metal salt of the metal constituent and a compound of the non-metal constituent, comprising introducing a metal salt of the metal constituent in the vapor phase and a non-metal constituent in the vapor phase into a liquid alkali metal or a liquid alkaline earth metal such that ceramic is formed from the metal constituent and the non-metal constituent within a liquid metal environment.
2. The method of claim 1, wherein the metal constituent is selected from the group comprising Ti, Al, Zr, Ta, Si and mixtures thereof.
3. The method of claim 2, wherein the non-metal constituent is selected from the group consisting of C, B, N, S, Si and mixtures thereof.
4. The method of claim 3, wherein the ceramic is produced continuously.
5. The method of claim 3, wherein the liquid alkali metal or alkaline earth metal is substantially maintained at a temperature less than about 400°C during production of the ceramic.
6. The method of claim 3, wherein the metal salt is a halide.
7. The method of claim 3, wherein the metal salt is a chloride.
8. The method of claim 6, wherein the liquid alkali metal is Na, K or mixtures thereof.
9. The method of claim 6, wherein the liquid alkaline earth metal is Ca, Ba, Mg or mixtures thereof.
10. The method of claim 3, wherein the liquid alkali metal is Na and the liquid alkaline earth metal is Mg and the metal halide is a chloride.

11. The method of claim 1, wherein the non-metal constituent contains carbon to produce a ceramic carbide.

12. The method of claim 1, wherein the non-metal constituent contains boron to produce a ceramic boride.

13. The method of claim 1, wherein the non-metal constituent contains nitrogen to produce a ceramic nitride.

14. The method of claim 1, wherein the non-metal constituent contains both carbon and boron.

15. The method of claim 1, wherein the non-metal constituent is C_2N_2 .

16. The method of claim 1, wherein the non-metal constituent contains silicon to produce a ceramic silicide.

17. The method of claim 1, wherein the non-metal constituent contains sulfur to produce a ceramic sulfide.

18. The method of claim 1, wherein the ceramic is formed in the presence of excess liquid metal.

19. The method of claim 1, wherein the metal constituent is selected from the group comprising Ti, Al, Zr, Ta, Si and mixtures thereof; the non-metal constituent is selected from the group comprising C, B, N, Si, S and mixtures thereof; the metal salt is a halide; the liquid alkali metal is Na, K, or mixtures thereof, and the liquid alkaline earth metal is Ca, Mg or mixtures thereof.

20. The method of claim 19, wherein the metal salt and non-metal constituent are introduced into the liquid in the vapor phase at a pressure in the range of from about 2 to about 10 atmospheres.

21. The method of claim 19, wherein the metal salt and non-metal constituent are introduced into the liquid metal in the vapor phase at a velocity not less than the sonic velocity of the vapor.

22. A ceramic produced by the method of claim 1.

23. A ceramic produced by the method of claim 19.

24. A method of continuously producing a non-oxide ceramic formed of a metal constituent and a non-metal constituent, comprising introducing a salt of the metal constituent in the vapor phase and a non-metal constituent in the vapor phase into a liquid alkali metal or a liquid alkaline earth metal or mixtures thereof to react the vapor constituents with liquid metal subsurface of the liquid metal to form ceramic particles, the liquid metal being present in excess of the stoichiometric amount necessary to convert the constituents into ceramic particles to absorb sufficient heat of reaction to prevent the ceramic particles from sintering, separating the ceramic particles from the excess liquid metal and recycling unused liquid alkali metal or liquid alkaline earth metal.

25. The method of claim 24, wherein the salt of the metal constituent in the vapor phase and the non-metal constituent in the vapor phase are mixed in the vapor phase and thereafter introduced into the liquid metal at a velocity not less than the sonic velocity of the mixed vapor.

26. The method of claim 25, wherein the mixed vapor is introduced into the liquid metal at a pressure in the range of from about 2 atmospheres to about 10 atmospheres.

27. The method of claim 4, wherein the vapor constituents are diluted with an inert gas.

28. The method of claim 24, wherein the liquid metal is flowing in a stream and the metal constituent vapor with the non-metal constituent vapor are introduced subsurface into the stream of liquid metal.

29. The method of claim 28, wherein the salt of the metal constituent and the non-metal constituent are introduced into the flowing stream of liquid metal as a vapor having a velocity not less than the sonic velocity of the vapor.

30. The method of claim 29, wherein the liquid metal is Na.

31. The method of claim 28, wherein the metal constituent is selected from the group comprising Ti, Al, Zr, Ta, Si and mixtures thereof and the non-metal constituent is selected from the group comprising C, B, N, Si, S and mixtures thereof.

32. The method of claim 31, wherein the salt of the metal constituent is a halide and the liquid metal is an alkali metal.

33. The method of claim 32, wherein the non-metal constituent is CCl_4 .

34. The method of claim 32, wherein the non-metal constituent is BCl_3 .

35. The method of claim 32, wherein the non-metal constituent is a combination of C and N.

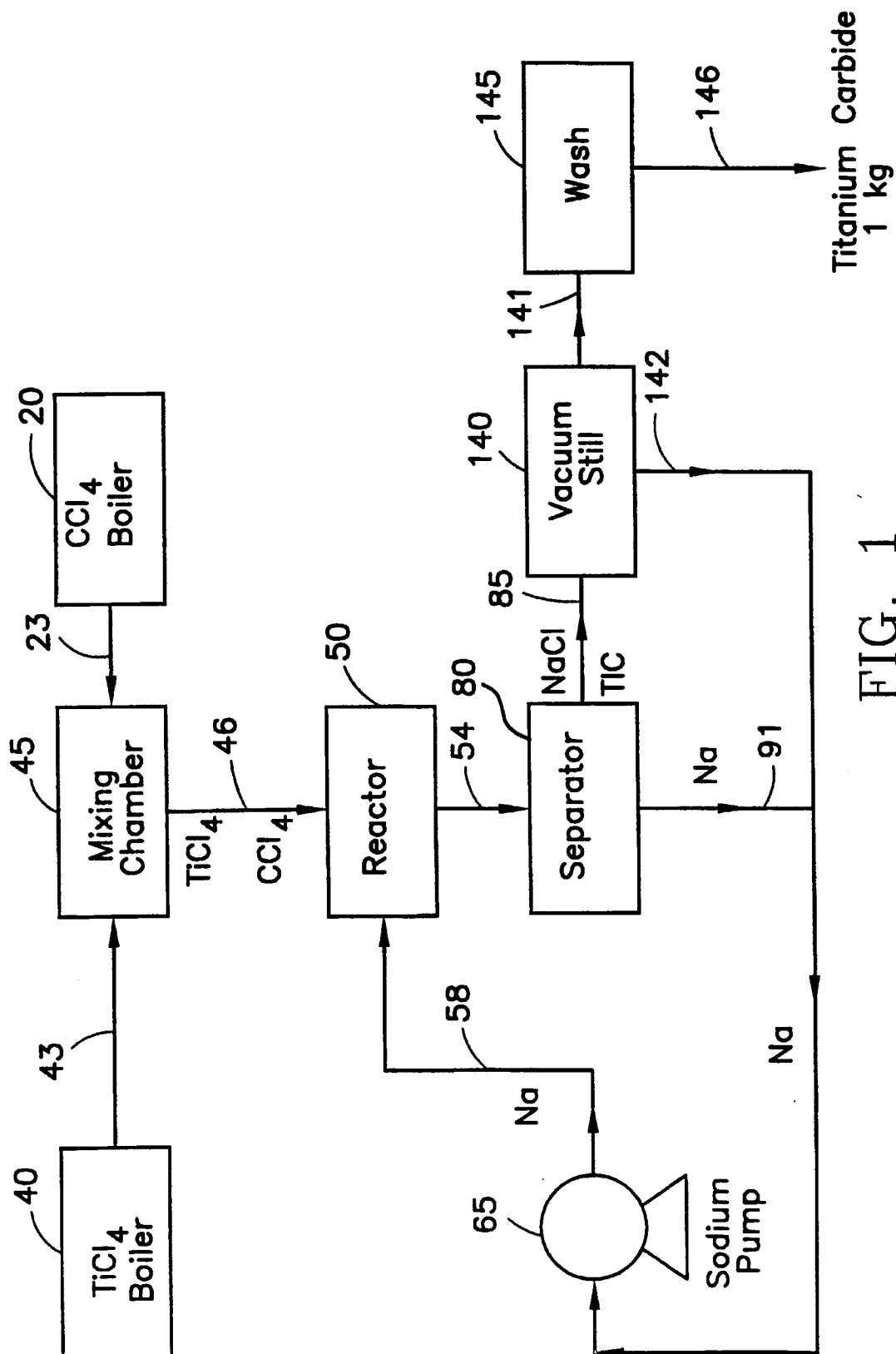
36. The method of claim 32, wherein the non-metal constituent contains nitrogen.

37. The method of claim 32, wherein the non-metal constituent contains silicon.

38. The method of claim 32, wherein the non-metal constituent contains S.

39. A ceramic made by the method of claim 24.

1/3



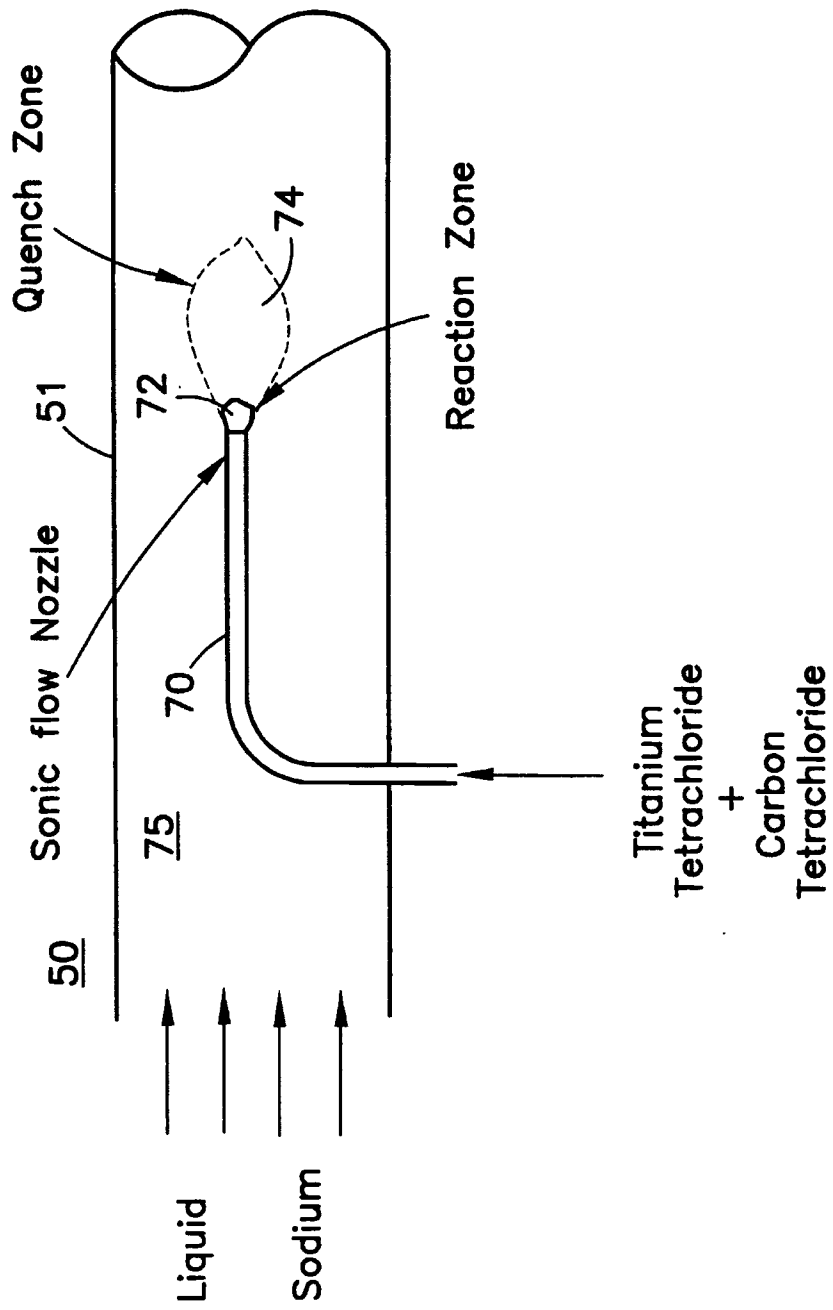


FIG. 2

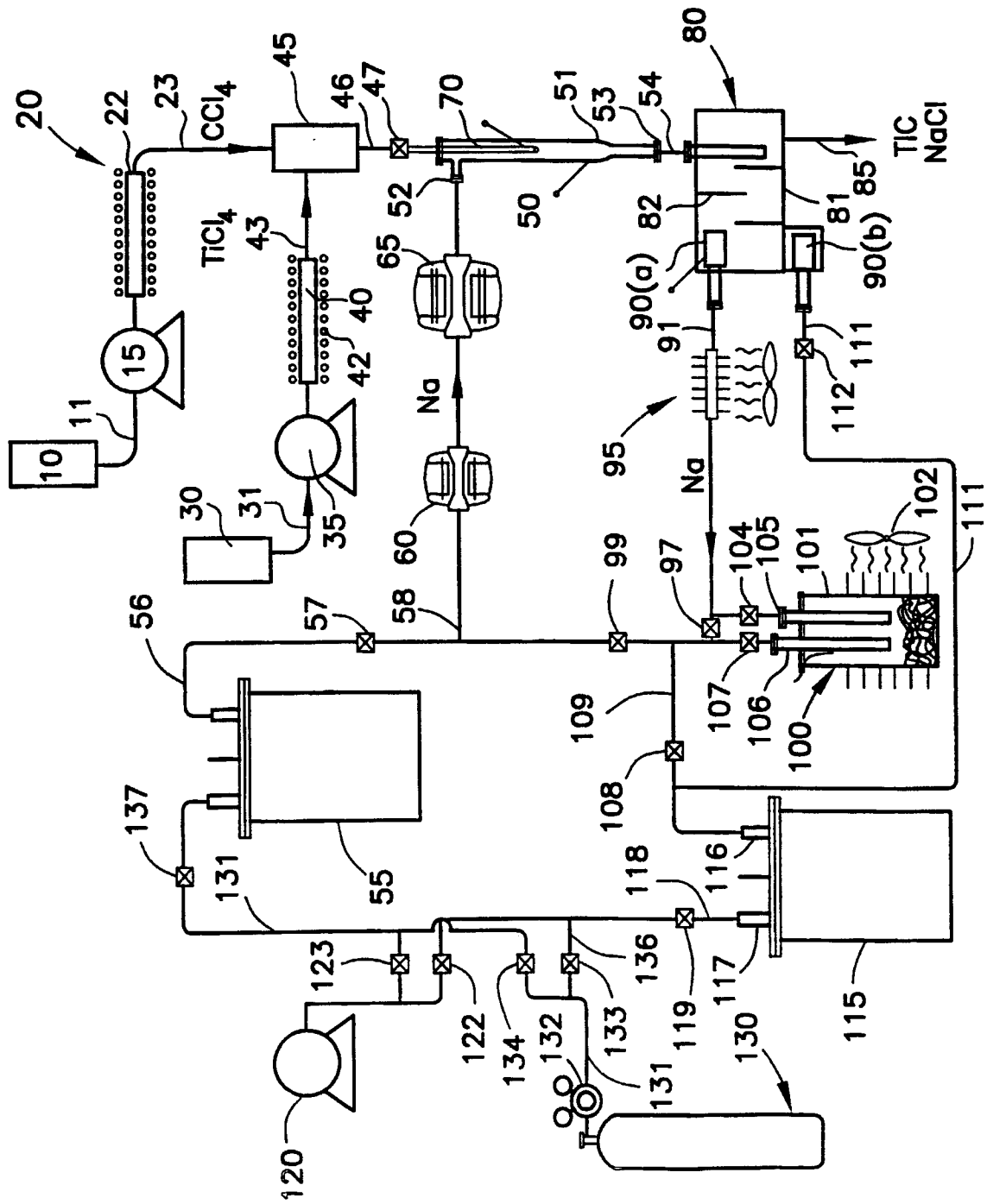


FIG. 3

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
12 May 2005 (12.05.2005)

PCT

(10) International Publication Number
WO 2005/042792 A1

(51) International Patent Classification⁷: **C22B 34/12**,
5/04, B30B 9/14, 9/12, B29C 47/08

(74) Agent: **LEVY, Harry, M.**; Emrich & Dithmar, LLC.,
Suite 2080, 125 South Wacker Drive, Chicago, IL 60606
(US).

(21) International Application Number:
PCT/US2004/033823

(22) International Filing Date: 14 October 2004 (14.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/692,096 22 October 2003 (22.10.2003) US

(71) Applicant (for all designated States except US): **INTER-
NATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

(72) Inventors; and

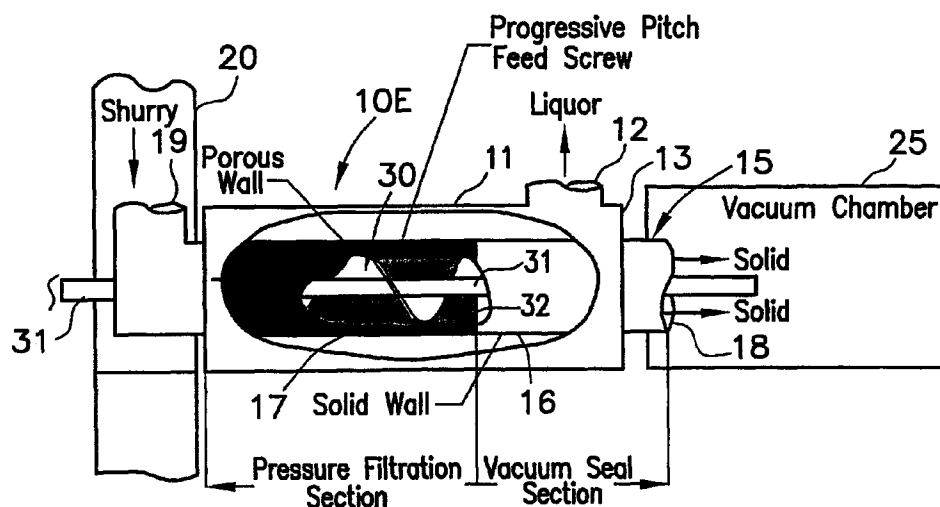
(75) Inventors/Applicants (for US only): **ARMSTRONG,
Donn, Reynolds** [US/US]; 6005 Ridge Court, Lisle, IL
60532 (US). **ANDERSON, Richard, P.** [US/US]; 5836
Sunrise Avenue, Clarendon Hills, IL 60514 (US). **JACOB-
SEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL
60447 (US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: FILTER EXTRACTION MECHANISM



(57) Abstract: A transfer mechanism between a first vessel containing a slurry of liquid and solids and a second vessel with at least one of said first and second vessels being under a protective atmosphere and/or vacuum. There is a housing in communication with the first and second vessels with a screw having at least one helical thread along the longitudinal shank within the housing for transferring material between vessels. The slurry entering the housing from the first vessel has the solids therein concentrated as the slurry is transported toward the second vessel while liquid is expressed from the slurry until the concentrated solids form a plug isolating the two second vessels as solids discharge into the second vessel.



Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

FILTER EXTRACTION MECHANISM

RELATED APPLICATIONS

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on non-provisional application Serial No. 10/692,096 filed October 22, 2003, which application according to 35 U.S.C. §365(c), is a continuation-in-part of PCT application serial no. PCT/US03/27647, filed September 3, 2003, which pursuant to 35 U.S.C. 119(e), claims the priority based on Provisional Application Serial No. 60/408,919 filed September 7, 2002.

BACKGROUND OF THE INVENTION

This invention relates to the Armstrong process as described in 5,779,761, 5,958,106 and 6,409,797, the disclosures of each of which is incorporated herein by reference. In the practice of the invention disclosed in the above referenced patents, there is produced in the reaction chamber a slurry consisting of excess reductant metal, salt particles produced and elemental material or alloy particles or powder produced. This slurry is thereafter treated by a variety of methods. However, all of the methods have in common the separation of excess liquid metal from the slurry and thereafter separating the remaining liquid metal and the produced salt from the desired product which is the elemental material or alloy. In the particular example disclosed in the three referenced patents, liquid sodium is used as a reductant for titanium tetrachloride to produce titanium powder.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a transfer mechanism and method for transferring a slurry of liquid and particles between two vessels or containers, at least one of which is under vacuum or inert atmosphere.

Yet another object of the present invention is to provide a transfer mechanism of the type set forth for the Armstrong Process in order to transfer slurry from an inerted vessel or container to a vacuum or inerted chamber for further processing wherein a plug established in the transfer mechanism isolating the vessels or containers.

Yet another object of the present invention is to provide a transfer mechanism between a first vessel containing a slurry of liquid and solids and a second vessel with at least one of the first and second vessels being under a protective atmosphere and/or vacuum, comprising a housing in communication with the first and the second vessels, a screw having at least one helical thread along a longitudinal shank within the housing for transferring material from the first vessel to the second vessel, the screw and the housing cooperating to compress the slurry, whereby slurry entering the housing from the first vessel has the solids therein concentrated as the slurry is transported by the screw toward the second vessel while liquid is expressed from the slurry as the solids are concentrated until the concentrated solids form a plug isolating the second vessel from the first vessel while solids discharge into the second vessel.

A further object of the invention is to provide a transfer mechanism between a first vessel containing a slurry of liquid alkali or alkaline earth metal or mixtures thereof and metal or alloy or ceramic particles and halide salt particles and a second vessel with at least one of the first and second vessels having a protective atmosphere and/or

vacuum therein, comprising a housing in communication with the first and the second vessels, a screw having at least one helical thread along a longitudinal shank within the housing for transferring material from the first vessel to the second vessel, the screw and the housing cooperating to increase the concentration of solids in the slurry between the first and the second vessels until the concentrated particles form a plug isolating the second vessel and the protective atmosphere or vacuum therein from the first vessel and the protective atmosphere or vacuum therein while solids discharge into the second vessel.

A final object of the present invention is to provide a method of concentrating and transferring a slurry of a liquid and solids from one container to another while isolating the environments within the containers from each other, comprising providing communication between the containers, transporting slurry from one container toward another container while expressing liquid from the slurry thereby increasing the solids concentration thereof until a plug is formed between two containers isolating same while solids from the plug are transferred to the another container.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantage of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an

inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a schematic illustration showing the two vessels and an embodiment of the transfer mechanism therebetween;

FIG. 2 is a schematic illustration of an alternate embodiment of the present invention;

FIG. 3 is a schematic illustration of yet another embodiment of the present invention; and

FIG. 4 is a schematic illustration of a further embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to Fig. 1 of the drawings, there is shown a transfer mechanism 10 which includes a double walled conduit including an outer conduit wall 11 having a liquid outlet 12 and end walls 13, the wall 11 being preferably but not necessarily cylindrical. Interior of the cylindrical wall 11 is an inner tube or conduit 15 having a portion 16 which is solid and a portion 17 which is apertured and may be a mesh of any suitable size. The inner tube or conduit 15 may either be cylindrical as illustrated in Fig. 1 or conical as will be explained, the inner conduit 15 has a discharge end 18 thereof which opens into a vacuum chamber 25 and has an inlet end 19 thereof which opens into a container or vessel 20 in communication with the reactor as illustrated in the Armstrong patents previously referenced and incorporated herein.

A feed screw 30 is positioned within the inner conduit 15 and includes a rotatable

shank 31 having a helical thread 32 positioned on the shank 31 as is well known in the art. The thread 32 may have a constant or a variable pitch. The pitch is the distance between adjacent threads and the variable pitch may preferably be a progressive pitch in which the pitch decreases from the vessel 20 toward the container or vessel 25, for a purpose hereinafter described.

In the preferred but not limiting embodiment of the present invention, the transfer mechanism 10 is used in conjunction with a material made by the Armstrong Process. More particularly, for purposes of illustration only, the slurry discussed herein will be a combination of liquid sodium, sodium chloride particles and particles of titanium and/or a titanium alloy. As set forth in the Armstrong patents, a variety of metal and non-metal products may be made thereby and it is intended that the present invention not be limited to any particular product made by the Armstrong Process and certainly not limited to the preferred product described herein.

In any event, the vessel or container 20 preferably operated under an inert atmosphere or under vacuum has therein a slurry of the particles previously described and as the slurry enters the portion 19 of the inner conduit or tube 15 and the feed screw 30 is rotated as illustrated in the drawings by rotation of the shank 31, the slurry is moved along the feed screw from left to right as illustrated in Fig. 1. Because of the progressive pitch of the feed screw 30 in Fig. 1, that is the threads 32 thereof are closer together so that the pitch decreases from left to right, the solid material is concentrated as it is moved from the container or vessel 20 to the container or vessel 25. Moreover, because the portion 17 of the conduit or tube 15 is apertured or porous, liquid sodium drains therethrough and passes out of the outlet 12 for further processing. Therefore,

the slurry as it is transported from container or vessel 20 to container or vessel 25 becomes more concentrated as liquid is drained therefrom and the density increases as the pitch between the adjacent threads diminishes.

Another way to express what occurs is that the volume between adjacent threads and the wall of the cylinder or tube 16 diminishes as material is moved by the feed screw 30 from container or vessel 20 to container or vessel 25. By the time the slurry is concentrated and reaches the portion 16, the solid portion 16 of the inner tube or conduit 15, a seal or plug is established between the vessel 25 and the vessel 20 which houses the slurry from the reactor thereby isolating the two vessels and the respective environments therein, one from the other. By isolating, we mean nearly complete separation of the two environments, not necessarily perfect separation, although perfect is desirable. The formation of a seal by the transfer mechanism 10 is a critical aspect of the present invention because separation of liquid sodium and salt from the desired particles of the ceramic or metal alloy, as described in the Armstrong patents may include distillation in a vacuum chamber or a vessel 25 or removal of the liquid metal by vaporization with a hot inert sweep gas and the Armstrong reactor itself may be an inerted vessel such as with argon. Accordingly, it is important for a seal or plug to be formed between the two containers or vessels in order to permit continuous operation between the two vessels without the necessity of shutting down one of the vessels during transfer or destroying the protective atmosphere in the vessel 20 or the vacuum or protective atmosphere in vessel 25.

Referring to Figs. 2 and 3, there are disclosed alternate embodiments of the invention. Again with the principle feature that the volume between adjacent screw

threads and the container or housing in which the feed screw is positioned diminishes from vessel 20A to vessel 25A. As seen in Fig. 2, the transfer mechanism 10A has a housing 15A conical in shape and the screw 30 therein may or may not be a progressive pitch screw. The screw threads in the embodiment illustrated in Fig. 2 may not need to be closer together, that is the pitch need not be diminished in order to reduce the volume of the material between adjacent threads and the housing wall as the material is moved from left to right or from vessel 20A to vessel 25A. However, it may be advantageous to use both the conical shaped inner housing 15A with or without a progressive screw 30A depending on engineering considerations.

Referring to Fig. 3, there is shown another embodiment of the present invention in which the shank 31B of the screw 30B is conical in shape with the larger end of the cone being adjacent the vessel 25B and with the pitch between adjacent threads 32B being constant or diminishing. In either case, the volume of the area between adjacent threads and the inner container 15B diminishes as the material is moved from the vessel 20B to the vessel 25B.

Referring to Fig. 4, there is shown a further embodiment 10C of the present invention in which a cylinder 15C interconnects vessels 20C and 25C and transports slurry while concentrating same between the two vessels. Slurry entering the inlet 19C of the cylinder 15C is concentrated upon rotation of screw 30C due to movement of the helical thread 32C upon rotation of the shaft 31C. The outlet end 18C of cylinder 15C is an apertured plate having an effective diameter smaller than the inlet 19C thereby restricting flow of the slurry causing in cooperation with the screw 30C and housing or cylinder 15C the solids in the slurry to concentrate while liquid is expressed from the

slurry and is separated therefrom through outlet or drain 12C. As solids concentrate at the outlet end 18C, a plug is formed which isolates, as hereinbefore explained, vessel 20 from vessel 25, thereby permitting the continuous production of slurry in vessel 20, or a vessel or container in communication therewith, and continuous separation of solids, even if wet with liquid, by the transfer mechanism 10C in vessel 25 or a vessel in communication therewith for further treatment in the same or different environment as vessel 20.

By way of example only, in the production of Ti or a Ti alloy by the reduction of TiCl_4 with Na in an inert atmosphere as taught in the incorporated Armstrong patents, separation of Na and/or NaCl from Ti or Ti alloy powder in vessel 25 may be accomplished by distillation and/or by a hot inert sweep gas followed by passivation and/or washing the water. By effectively separating the environments in vessels 20 and 25, continuous operation of production and separation is accomplished, an important commercial feature. In one example of the invention, liquid Na may be present at about 60% by weight of the slurry leaving vessel 20, while the wet solids discharged into vessel 25 may have Na present only in the range of from about 20 to about 50% by weight.

Although the invention has been described with respect to an inerted vessel and a vacuum vessel, the invention includes movement and concentration of material from one container to another without compromising the environment of either container. The containers may be connected pipes or vessels, and the environments may be vacuums, inerted atmospheres or otherwise. Central to the invention is concentration of solids in a slurry to transport solids from one environment to another while forming

a seal or plug therebetween so as to isolate the environments from each other.

While there has been disclosed what is considered to be the preferred embodiment of the present invention, it is understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

WHAT IS CLAIMED IS:

1. A transfer mechanism between a first vessel containing a slurry of liquid and solids and a second vessel with at least one of said first and second vessels being under a protective atmosphere and/or vacuum, comprising a housing in communication with said first and said second vessels, a screw having at least one helical thread along a longitudinal shank within said housing for transferring material from said first vessel to said second vessel, said screw and said housing cooperating to compress the slurry, whereby slurry entering said housing from said first vessel has the solids therein concentrated as the slurry is transported by said screw toward said second vessel while liquid is expressed from the slurry as the solids are concentrated until the concentrated solids form a plug isolating said second vessel from said first vessel while solids discharge into said second vessel.
2. The transfer mechanism of claim 1, wherein the volume between adjacent screw threads and said housing diminishes between said first and said second vessels.
3. The transfer mechanism of claim 1, wherein said screw is a variable pitch screw.
4. The transfer mechanism of claim 1, wherein said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.
5. The transfer mechanism of claim 1, wherein said housing is generally cylindrical.
6. The transfer mechanism of claim 1, wherein said housing is conical with the smallest end being nearest said second vessel.

7. The transfer mechanism of claim 1, wherein said housing has an inlet with a first diameter and an outlet with a second diameter near said second vessel, said outlet being smaller than said inlet.

8. The transfer mechanism of claim 1, wherein said housing is cylindrical having the end in communication with said second vessel restricting flow of concentrated solids from said housing to said second vessel.

9. The transfer mechanism of claim 1, wherein said housing near said second vessel has a restriction therein.

10. The transfer mechanism of claim 9, wherein the restriction in said housing is an apertured plate in the end of said housing in communication with said second vessel.

11. The transfer mechanism of claim 1, wherein said housing is cylindrical and said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

12. The transfer mechanism of claim 1, wherein said housing is conical with the smallest end being nearest said second vessel and said screw has threads of constant pitch.

13. The transfer mechanism of claim 1, wherein said shank has an increasing diameter toward said second vessel.

14. The transfer mechanism of claim 1, wherein at least a part of said housing in communication with said first vessel has a plurality of apertures therein.

15. The transfer mechanism of claim 14, wherein the plurality of apertures is a mesh.

16. The transfer mechanism of claim 1, and further comprising an outlet in said housing for separating liquid expressed from the slurry from the concentrated solids.

17. A transfer mechanism between a first vessel containing a slurry of liquid alkali or alkaline earth metal or mixtures thereof and metal or alloy or ceramic particles and halide salt particles and a second vessel with at least one of said first and second vessels having a protective atmosphere and/or vacuum therein, comprising a housing in communication with said first and said second vessels, a screw having at least one helical thread along a longitudinal shank within said housing for transferring material from said first vessel to said second vessel, said screw and said housing cooperating to increase the concentration of solids in the slurry between said first and said second vessels until the concentrated particles form a plug isolating said second vessel and the protective atmosphere or vacuum therein from said first vessel and the protective atmosphere or vacuum therein while solids discharge into said second vessel.

18. The transfer mechanism of claim 17, wherein said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

19. The transfer mechanism of claim 17, wherein said housing is generally cylindrical.

20. The transfer mechanism of claim 17, wherein said housing is conical with the smallest end being nearest said second vessel.

21. The transfer mechanism of claim 17, wherein said housing is cylindrical and said screw is a progressive pitch screw with the smallest pitch being nearest said second vessel.

22. The transfer mechanism of claim 17, wherein said housing is conical with the smallest end being nearest said second vessel and said screw has threads of constant pitch.

23. The transfer mechanism of claim 17, wherein said shank has an increasing diameter toward said second vessel.

24. The transfer mechanism of claim 17, wherein at least a part of said housing in liquid communication with said first vessel has a plurality of apertures therein.

25. The transfer mechanism of claim 24, wherein the plurality of apertures is a mesh.

26. The transfer mechanism of claim 17, and further comprising an outlet in said housing for separating liquid from the solids in the slurry.

27. The transfer mechanism of claim 26, wherein a double wall housing is provided wherein the inner wall has a portion thereof apertured and a portion thereof solid and the outer wall has said outlet therein, said screw being positioned within said inner wall.

28. The transfer mechanism of claim 17, wherein said housing is cylindrical having the end in communication with said second vessel restricting flow of concentrated solids from said housing to said second vessel.

29. The transfer mechanism of claim 17, wherein said housing near said second vessel has a restriction therein.

30. The transfer mechanism of claim 29, wherein the restriction in said housing is an apertured plate at or near the end of said housing in communication with said second vessel.

31. A method of concentrating and transferring a slurry of a liquid and solids from one container to another while isolating the environments within said containers from each other, comprising providing communication between the containers, transporting slurry from one container toward another container while expressing liquid from the slurry thereby increasing the solids concentration thereof until a plug is formed between two containers isolating the containers while solids from the plug are transferred to the another container.

32. The method of claim 31, wherein at least one container is operated under an inert atmosphere.

33. The method of claim 31, wherein at least one container is operated under vacuum.

34. The method of claim 31, wherein the slurry contains liquid metal and metal particles.

35. The method of claim 34, wherein the slurry contains liquid alkali or alkaline earth metal.

36. The method of claim 34, wherein slurry contains liquid sodium metal and particles of Ti or an alloy thereof.

1/4

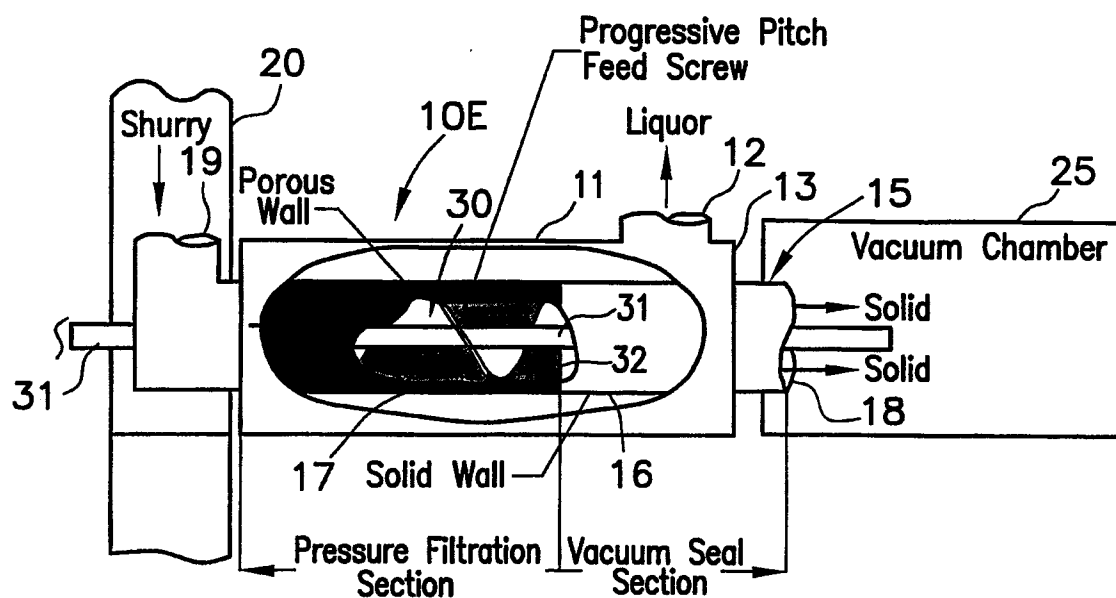


FIG.1

2/4

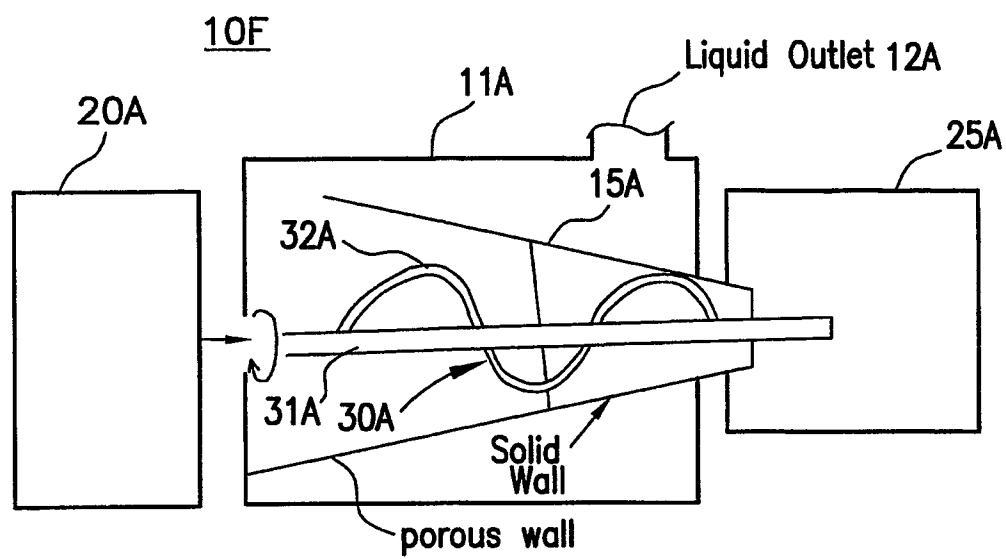


FIG. 2

3/4

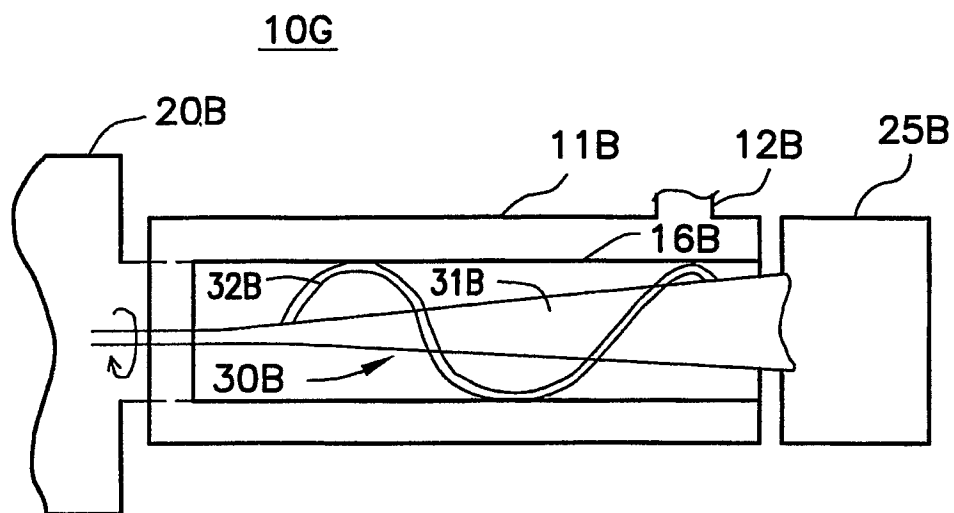
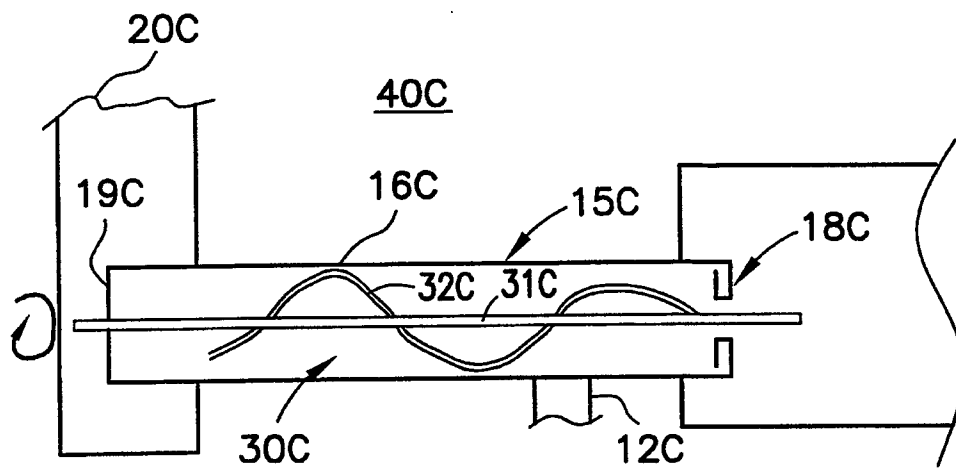


FIG.3

4/4



Comparison solids w/o changing volume

FIG.4

INTERNATIONAL SEARCH REPORT

In Application No
PCT/US2004/033823

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B34/12 C22B5/04 B30B9/14 B30B9/12 B29C47/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B30B B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2004/022798 A (ARMSTRONG DONN ; JACOBSEN LANCE (US); ANDERSON RICHARD (US); INTERNAT) 18 March 2004 (2004-03-18) the whole document	1-8, 11-28, 31-36
Y,P		9, 10, 29, 30
Y	US 4 839 120 A (BABA TOSHIO ET AL) 13 June 1989 (1989-06-13) column 2, line 57 - column 3, line 11; figure 1	1-36
Y	US 3 919 087 A (BRUMAGIM IVAN S) 11 November 1975 (1975-11-11) abstract; figure 1	1-6, 11-13, 15-27, 31-33
	----- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

12 January 2005

Date of mailing of the international search report

24/01/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Baumgartner, R

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/033823

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 130 (M-478), 14 May 1986 (1986-05-14) -& JP 60 255300 A (YAMATO SANGYO KK), 16 December 1985 (1985-12-16) abstract	1-36
Y	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) -& JP 11 090692 A (CHIYODA CORP;ISHIGAKI:KK), 6 April 1999 (1999-04-06) abstract	1-36
Y	US 5 958 106 A (ANDERSON RICHARD PAUL ET AL) 28 September 1999 (1999-09-28) cited in the application column 5, line 66 - column 7, line 23; figures 1,3,4	1,17, 34-36
Y	US 3 836 302 A (KAUKEINEN R) 17 September 1974 (1974-09-17) abstract column 1, line 55 - column 4, line 63 figures 1,2	9,10,29, 30

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No
PCT/US2004/033823

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2004022798	A	18-03-2004	WO 2004022798 A1	18-03-2004
US 4839120	A	13-06-1989	JP 1864415 C	08-08-1994
			JP 5079001 B	01-11-1993
			JP 63207612 A	29-08-1988
			BE 1001673 A3	06-02-1990
			DE 3805569 A1	01-09-1988
US 3919087	A	11-11-1975	NONE	
JP 60255300	A	16-12-1985	NONE	
JP 11090692	A	06-04-1999	NONE	
US 5958106	A	28-09-1999	US 5779761 A	14-07-1998
			US 2002148327 A1	17-10-2002
			US 2002152844 A1	24-10-2002
			US 2003145682 A1	07-08-2003
			US 2002005090 A1	17-01-2002
			US 2004166045 A1	26-08-2004
			US 2003061907 A1	03-04-2003
			AU 686444 B2	05-02-1998
			AU 3320195 A	04-03-1996
			BR 9508497 A	23-12-1997
			CA 2196534 A1	15-02-1996
			CN 1161064 A ,B	01-10-1997
			DE 69521432 D1	26-07-2001
			DE 69521432 T2	29-05-2002
			EP 0777753 A1	11-06-1997
			ES 2161297 T3	01-12-2001
			JP 10502418 T	03-03-1998
			JP 3391461 B2	31-03-2003
			KR 241134 B1	02-03-2000
			NO 970444 A	26-03-1997
			RU 2152449 C1	10-07-2000
			WO 9604407 A1	15-02-1996
US 3836302	A	17-09-1974	CA 1015912 A1	23-08-1977
			DE 2313243 A1	11-10-1973
			FR 2178946 A1	16-11-1973
			GB 1405619 A	10-09-1975
			SE 382170 B	19-01-1976

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
19 April 2007 (19.04.2007)

PCT

(10) International Publication Number
WO 2007/044635 A2

(51) International Patent Classification:

B22F 9/28 (2006.01) **C22C 1/04** (2006.01)
C22B 34/12 (2006.01) **C22C 14/00** (2006.01)

(21) International Application Number:

PCT/US2006/039331

(22) International Filing Date: 6 October 2006 (06.10.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/724,166 6 October 2005 (06.10.2005) US

(71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).
BENISH, Adam, John [US/US]; 1918 Highland Avenue, Crest Hill, IL 60435 (US).

(74) Agent: **LEVY, Harry, M.**; **EMRICH AND DITHMAR, LLC**, 125 South Wacker Drive, Suite 2080, Chicago, IL 60606 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

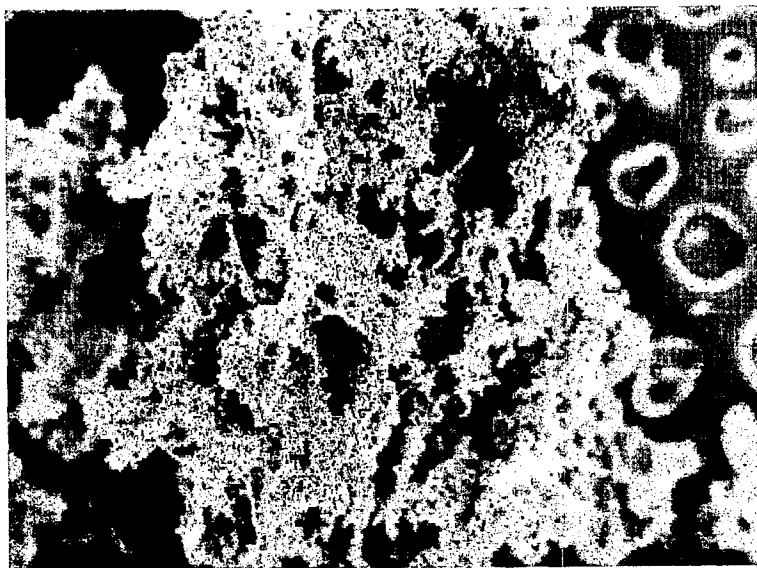
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TITANIUM BORIDE



Width(μm): 2600.44 Height(μm): 1950.33 μm/pixel: 1.270
Scope magnification: 50X

(57) Abstract: A titanium metal or a titanium alloy having submicron titanium boride substantially uniformly dispersed therein and a method of making same is disclosed. Ti powder of Ti alloy powder has dispersed within the particles forming the powder titanium boride which is other than whisker-shaped or spherical substantially uniformly dispersed therein.

TITANIUM BORIDE

Related Applications

This application, pursuant to 37 C.F.R. 1.78(c), claims priority based on provisional application serial No. 60/724,166 filed October 6, 2005.

BACKGROUND OF THE INVENTION

Relatively small boron additions to conventional titanium alloys provide important improvements in strength, stiffness and microstructural stability. Because boron is essentially insoluble in titanium at all temperatures of interest, the titanium boride is formed for even very small boron additions. The density of titanium boride is nearly equal to those of conventional Ti alloys, but its stiffness is over four times higher than conventional titanium alloys. Thus, titanium boride offers significant improvements in stiffness, tensile strength, creep, and fatigue properties. Since titanium boride is in thermodynamic equilibrium with titanium alloys, there are no interfacial reactions to degrade properties at elevated temperature. Further, because the coefficient of thermal expansion of titanium boride is nearly equal to values for titanium alloys, residual stresses are nearly eliminated" Taken from JOM Article May 2004 "Powder Metallurgy Ti-6Al-4V Alloys: Processing, Microstructure, and Properties", the entire disclosure of which is incorporated by reference.

Currently two approaches appear to be used to accomplish boron addition; 1) Blended elemental addition of TiB_2 and solid state reaction to produce the titanium boride which usually forms as whiskers with a 10 to 1 aspect ratio and 2) Pre-alloyed powders from a melt process.

Negatives of the blended elemental approach are the added effort to blend the powders to obtain a uniform distribution (which is never perfect) and the added time and temperature it takes the solid state reaction to transform TiB_2 to TiB (1300C for 6 hours). Also, this approach has the potential to form larger Titanium boride particles or have residual titanium boride particles that adversely affect properties. The titanium boride whiskers that are formed can lead to anisotropic properties of the part depending on the type of process used to make the part.

A negative of the pre-alloyed approach is that it has a tendency to leave large primary borides in the pre-alloyed materials that cause low fracture toughness.

Representative examples of patents related to producing metal alloys with titanium boride are the Davies et al. U.S. patent no. 6,099,664 issued to Davies et al. August 8, 2000, in which titanium boride particles in the 1-10 micron size range are produced in a molten reaction zone. The Blenkinsop et al. U.S. patent no. 6,488,073 issued December 3, 2002 teaches the addition of an alloy in which tantalum boride or tungsten boride particles are added to a molten alloy material to form a molten mixture which upon cooling has the boride distributed therein. Another method of making boride containing titanium alloys is disclosed in the Abkowitz U.S. patent no. 5,897,830 in which titanium boride powders are mixed with the powders of various constituents to form a consumable billet which is thereafter cast or melted to form the article of manufacture. Each of these processes as described in the above-mentioned patents has a variety of shortcomings, not the least of which is the imperfect distribution of the boride as well as the size of the boride particles.

SUMMARY OF THE INVENTION

The Armstrong Process as disclosed in U.S. Patent Nos. 5,779,761, 5,958,106 and 6,409,797, the entire disclosures of which are herein incorporated by reference appears very unexpectedly to give uniform distribution of very fine submicron titanium boride within the Ti or Ti alloy powder. This eliminates the need for blending and solid state reaction to form titanium boride; it also eliminates concerns regarding larger particles that can adversely affect fracture toughness and other mechanical properties. Because of the fineness of the titanium boride particles and the uniform distribution in most if not substantially all of the particles forming the powder, more isotropic mechanical properties may be achievable. None of the current approaches to boron addition to Ti powder can achieve this type of distribution of titanium boride, particularly in the submicron size ranges.

Accordingly, it is a principal object of the present invention to provide a titanium metal or a titanium alloy having submicron titanium boride substantially uniformly dispersed therein.

Another object of the invention is to provide a Ti powder or a Ti base alloy powder having submicron titanium boride substantially uniformly dispersed therein, wherein the Ti powder or Ti base alloy powder and titanium boride are made by the subsurface reduction of TiCl_4 and a boron halide and other chlorides and/or halides

of the Ti base alloy constituents, if present, with liquid alkali or alkaline earth metal or mixtures thereof in a reaction zone.

A further object of the invention is to provide a Ti powder or a Ti base alloy powder having submicron titanium boride which is other than whisker-shaped or spherical substantially uniformly dispersed therein.

A final object of the invention is to provide a product having an SEM substantially as shown in one or more of Figures 1- 8.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is an SEM of a titanium powder having submicron titanium boride substantially uniformly dispersed therethrough at a magnification of 50;

FIG. 2 is another SEM of a titanium powder having submicron titanium boride substantially uniformly dispersed therethrough at a magnification of 50;

FIG. 3 is a similar SEM of a titanium powder having submicron titanium boride substantially uniformly dispersed therethrough at a magnification of 3000;

FIG. 4 is another SEM of a titanium powder having submicron titanium boride substantially uniformly dispersed therethrough at a magnification of 3000;

FIG. 5 is a titanium base alloy having about 10% total of aluminum and vanadium with titanium boride with submicron titanium borides substantially uniformly dispersed throughout the particles forming the powder at a 40 magnification;

FIG. 6 is a titanium base alloy having about 10% total of aluminum and vanadium with titanium boride with submicron titanium borides substantially

uniformly dispersed throughout the particles forming the powder at a 50 magnification;

FIG. 7 is a titanium base alloy having about 10% total of aluminum and vanadium with titanium boride with submicron titanium borides substantially uniformly dispersed throughout the particles forming the powder at a 3000 magnification;

FIG. 8 is a titanium base alloy having about 10% total of aluminum and vanadium with titanium boride with submicron titanium borides substantially uniformly dispersed throughout the particles forming the powder at a 3000 magnification (a different portion of the same sample as Fig. 7).

DESCRIPTION OF THE PREFERRED EMBODIMENT

Using the Armstrong method described in the above three identified patents and application Serial No. 11/186,724 filed July 21, 2005, the entire application is herein incorporated by reference.

The equipment used to produce the 6/4 alloy with submicron titanium boride substantially uniformly dispersed therein is similar to that disclosed in the aforementioned patents disclosing the Armstrong Process with the exception that instead of only having a titanium tetrachloride boiler 22 as illustrated in those patents, there is also a boiler for each constituent of the alloy connected to the reaction chamber by suitable valves. Boron addition is from a boiler for BCl_3 . The piping acts as a manifold so that the gases are completely mixed as they enter the reaction chamber and are introduced subsurface to the flowing liquid sodium, preferably at least at sonic velocity, as disclosed in the incorporated patents. Upon subsurface contact with the liquid metal the halides immediately and completely react exothermically to form a reaction zone in which the reaction products are produced. The flowing liquid metal preferably sodium, sweeps the reaction products away from the reaction zone maintaining the reaction products at a temperature below the sintering temperatures of the reaction products. It was determined during production of the 6/4 alloy that aluminum trichloride is corrosive and required special materials not required for handling either titanium tetrachloride or vanadium tetrachloride. Therefore, Hastelloy C-276 was used for the aluminum trichloride boiler and the piping to the reaction chamber. The BCl_3 is not as corrosive as AlCl_3 .

During most of the runs the steady state temperature of the reactor was maintained at about 400°C by the use of sufficient excess sodium. Other operating conditions for the production of the 6/4 alloy powder with submicron titanium boride dispersed in most, if not substantially all, of the particles forming the powder were as follows:

A device similar to that described in the incorporated Armstrong patents was used except that a VCl_4 boiler, a AlCl_3 boiler and a BCl_3 boiler were provided and all three gases were fed into the line feeding TiCl_4 into the liquid Na. The typical boiler pressures and system parameters are listed hereafter in Table 1.

TABLE 1

Run#	Boron Wt%	Aluminum Wt%	Vanadium Wt%	Oxygen Wt%	TiCl_4 Noz. Dia. (in)	TiCl_4 Press. (Kpa)	TiCl_4 Flow (Kg/min)	VCl_4 Press. (Kpa)	AlCl_3 Press. (Kpa)	Boron Noz. Dia. (in)
NR285	.82 .89 .9 .82	-	-	.485 .477 .605 .578	7/32	540	2.4	-	-	.040
NR286	2.21 3.17 3.15 3.18	-	-	.874 .875 .985 .969	7/32	500	2.3	-	-	.040
NR291	.25 .38	7.08 6.91	2.84 2.5	.346 .494	7/32	500	2.9	640	860	.040
NR292	2.58 2.49	7.46 7.72	3.79 3.59	1.06 1.33	7/32	510	2.2	620	850	.040
A-308	.71 .64	-	-	.304 .303	7/32	500	2.5	-	-	.040
A-328	1.24	-	-	.31	5/32	550	1.23	-	-	.040

Inlet Na temperature about 240°C

Reactor Outlet Temperature about 510 C

Na Flowrate about 40 kg/min

The reactor was generally operated for approximately 250 seconds injecting approximately 11 kg of TiCl_4 . The salt and titanium alloy solids were captured on a wedge wire filter and free sodium metal was drained away. The product cake containing titanium alloy, sodium chloride and sodium was distilled at approximately 100 milli - torr at 550 to 575°C vessel wall temperatures for 20 hours. Once all the sodium metal was removed via distillation, the trap was re-pressurized with argon gas and heated to 750°C and held at temperature for 48 hours. The vessel containing the salt and titanium alloy cake was cooled and the cake was passivated with a 0.7 wt % oxygen/argon mixture. After passivation, the cake was washed with deionized water and subsequently dried in a vacuum oven at less than 100°C.

Table 2 below sets forth a chemical analysis of various runs for both Ti as well as 6/4 alloy with submicron titanium boride substantially uniformly dispersed therein from an experimental loop running the Armstrong Process. As used herein, titanium boride means principally TiB but does not exclude minor amounts of TiB_2 or other borides.

Similarly, the process described herein produces a novel powder in which most, if not substantially all, of the particles forming the powder have submicron titanium boride dispersed therein. While the boride dispersion may not always be perfect in every particle, the titanium boride is very small, submicron, and generally uniformly dispersed within the particles forming the powder, whether the powder is titanium or a titanium alloy.

As seen from Table 2 below, the sodium levels for 6/4 with submicron titanium boride are very low while the sodium level for Ti with submicron titanium boride are somewhat higher, but still less than commercially pure titanium, without submicron titanium boride dispersed therein, made by the Armstrong Process, as described in the incorporated application.

As stated in the referenced application, the surface area of the 6/4 alloy compared to the CP titanium, as determined using BET Specific Surface Area analysis with krypton as the adsorbate is much larger than the CP titanium. The surface area of

the 6/4 alloy with titanium boride is even greater, that is the alloy powder with titanium boride was smaller in average diameter and more difficult to grow into larger particles than Ti alloy without titanium boride.

TABLE 2

<u>Al % by weight</u>	<u>V % by weight</u>	<u>B % by weight</u>	<u>Na</u>
9	5		0.0039
10	5		0.0026
8	5		0.001
7	2.2		0.017
8	1.8		0.0086
5.4	5.3		0.0015
7.3	4.7		0.002
14	3		0.018
7.75	5.2		0.009
9.6	6.8		0.0078
13	6.7		0.0092
9.2	0.009		0.014
6	4		0.0018
5.7	3.5		0.0018
5	2.2		0.0018
5.3	3.6		0.0052
7.2	4		0.014
		0.82	0.018
		0.89	0.023
		0.9	0.0047
		0.82	0.0028
		2.21	0.0047
		3.17	0.0076
		3.15	0.013
		3.2	0.012
7.08	2.84	0.25	0.0025
6.91	2.5	0.38	0.0024
7.46	3.79	2.58	0.0023
7.72	3.59	2.49	0.0077

The SEMs of Figs. 1-8 show that the 6/4 powder and/or Ti powder with submicron titanium boride distributed therein is "frillier" than the previously made 6/4 powder in the referenced application. Each of the figures references a run disclosed in Table 1 and represents samples taken from that run at different magnifications. As stated in the referenced application and as reported by Moxson et al., *Innovations in Titanium Powder Processing* in the Journal of Metallurgy May 2000, it is clear that by-product fines from the Kroll or Hunter Processes contain large amounts of undesirable chlorine which is not present in the CP titanium powder or alloy made by the Armstrong Process. Moreover, the morphology of the Hunter and Kroll fines, as previously discussed, is different from the CP powder or the 6/4 alloy powder or either with submicron titanium boride therein made by the Armstrong Process. Neither the Kroll nor the Hunter process has been adapted to produce 6/4 alloy or any alloy. Alloy powders have been produced by melting prealloyed stock and thereafter using either gas atomization or a hydride-dehydride process (MHR). The Moxson et al. article discloses 6/4 powder made in Tula, Russia and as seen from Fig. 2 in that article, particularly Figures 2c and 2d the powders made by Tula Hydride Reduction process are significantly different than those made by the Armstrong Process. Moreover, referring to the Moxson et al. article in the 1998 issue of the International Journal of Powder Metallurgy, Vol. 4, No. 5, pages 45-47, it is seen that the chemical analysis for the pre-alloy 6/4 powder produced by the metal-hydride reduction (MHD) process contains exceptional amounts of calcium and also is not within ASTM specifications for aluminum.

As is well known in the art, solid objects can be made by forming 6/4 or CP titanium powders into a near net shapes and thereafter sintering, see the Moxson et al. article and can also be formed by hot isostatic pressing, laser deposition, metal injecting molding, direct powder rolling or various other well known techniques. Therefore, the titanium alloy powder or titanium powder with submicron titanium boride dispersed substantially uniformly therein made by the Armstrong method may be formed into a

consolidated or a consolidated and sintered product or may be formed into a solid object by well known methods in the art and the subject invention is intended to cover all such products made from the powder of the subject invention.

There has been disclosed herein a titanium metal powder or a titanium base alloy powder having submicron titanium boride substantially uniformly dispersed therein.

The specific titanium alloy of the type set forth wherein Al and V are present in a minor amount by weight, but preferably ASTM Grade 5, as well as commercially pure titanium, ASTM Grade 2, both as disclosed in the incorporated patent application, Table 1 therein, with submicron titanium boride substantially uniformly dispersed therein have been disclosed, wherein boron is present up to about 4% by weight. The invention however, includes any weight of boron added. Preferably, alloys have at least 50% by weight titanium with titanium boride, preferably TiB, present in any required amount..

Any halide may be used in the process, as previously described, but chlorides are preferred because they are readily available and less expensive than other halides. Various alkali or alkaline earth metals may be used, i.e. Na, K, Mg, Ca, but Na is preferred.

Solid products are routinely made by a variety of processes from the powders described herein. Products made from powder produced by the Armstrong method including BCl_3 introduced into flowing liquid reducing metal produce superior hardness and other desirable physical properties are within the scope of this invention.

While the invention has been particularly shown and described with reference to a preferred embodiment thereof, it will be understood by those skilled in the art that several changes in form and detail may be made without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A titanium metal or a titanium alloy having submicron titanium boride substantially uniformly dispersed therein.
2. The titanium alloy of claim 1, wherein Al and V are present in a minor amount by weight.
3. The titanium alloy of claim 2, wherein Al and V are present at a total concentration of about 10% by weight.
4. The titanium alloy of claim 3, wherein Al is present at a concentration of about 6% by weight and V is present at a concentration of about 4% by weight.
5. The titanium metal or titanium alloy of claim 1, wherein boron is present up to about 4% by weight.
6. The titanium metal or titanium alloy of claim 1, wherein said metal or base alloy is a powder and titanium boride is dispersed within most of the particles forming the powder.
7. The titanium metal or titanium alloy of claim 6, wherein titanium boride is dispersed within substantially all of the particles forming the powder.
8. The titanium metal or titanium alloy of claim 1, wherein said titanium boride is other than whisker-shaped or spherical.
9. The titanium metal or titanium alloy of claim 1, wherein said titanium or titanium alloy having titanium boride dispersed therein are consolidated powders.
10. The titanium metal or titanium alloy of claim 1, wherein said titanium or titanium alloy having titanium boride dispersed therein is sintered powder.
11. The titanium metal or titanium alloy of claim 1, wherein said titanium or titanium alloy having titanium boride dispersed therein is a solid.
12. The titanium metal or titanium alloy of claim 1, wherein the titanium boride is principally TiB.

13. A Ti powder or a Ti base alloy powder having submicron titanium boride substantially uniformly dispersed therein,

wherein said Ti powder or Ti base alloy powder and titanium boride are made by the subsurface reduction of TiCl_4 and a boron halide and other chlorides and/or halides of the Ti base alloy constituents, if present, with liquid alkali or alkaline earth metal or mixtures thereof in a reaction zone.

14. The material of claim 13, wherein the alkali or alkaline earth metal or mixtures thereof is present in sufficient quantity to maintain the reduction products below the sintering temperature thereof away from the reaction zone.

15. The material of claim 14, wherein the alkali metal is sodium and the alkaline earth metal is magnesium or calcium.

16. The material of claim 15, wherein the liquid metal is present as a stream.

17. The material of claim 16, wherein the chlorides and/or halides are introduced into the liquid metal as a gas at sonic velocity or greater.

18. The material of claim 14, wherein the boron halide is a chloride.

19. The material claim 18, wherein boron chloride is BCl_3 .

20. The material of claim 13, wherein said Ti base alloy contains Al and V and titanium boride in at least most of the particles forming the powder.

21. The material of claim 20, wherein titanium boride is in substantially all of the particles forming the powder.

22. A Ti powder or a Ti base alloy powder having submicron titanium boride which is other than whisker-shaped or spherical substantially uniformly dispersed therein.

23. The titanium base alloy powder of claim 22 wherein Al and V are present in a minor amount by weight.

24. The titanium base alloy powder of claim 23, wherein Al and V are present at a total concentration of about 10% by weight.

25. The titanium base alloy powder of claim 24, wherein Al is present at a concentration of about 6% by weight and V is present at a concentration of about 4% by weight.

26. The titanium powder or titanium base alloy powder of claim 22, wherein boron is present up to about 4% by weight.

27. The titanium powder or titanium base alloy powder of claim 26, wherein titanium boride is in at least most of the particles forming the powder.

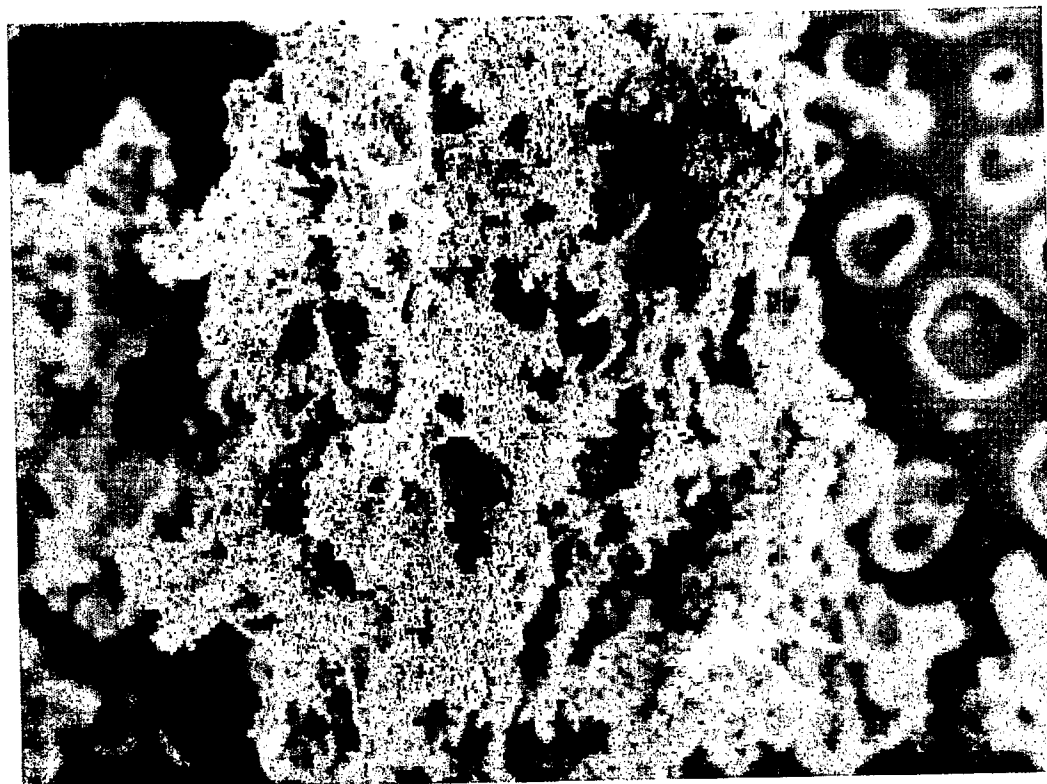
28. The titanium powder or titanium base alloy powder of claim 27, wherein the titanium boride is in substantially all of the particles forming the powder.

29. The Ti powder or titanium base alloy powder of claim 28, wherein substantially all of the titanium boride is TiB.

30. A product having an SEM substantially as shown in one or more of the Figures 1- 8.

1-8

File: Nr285.02 50 mag Ti-B

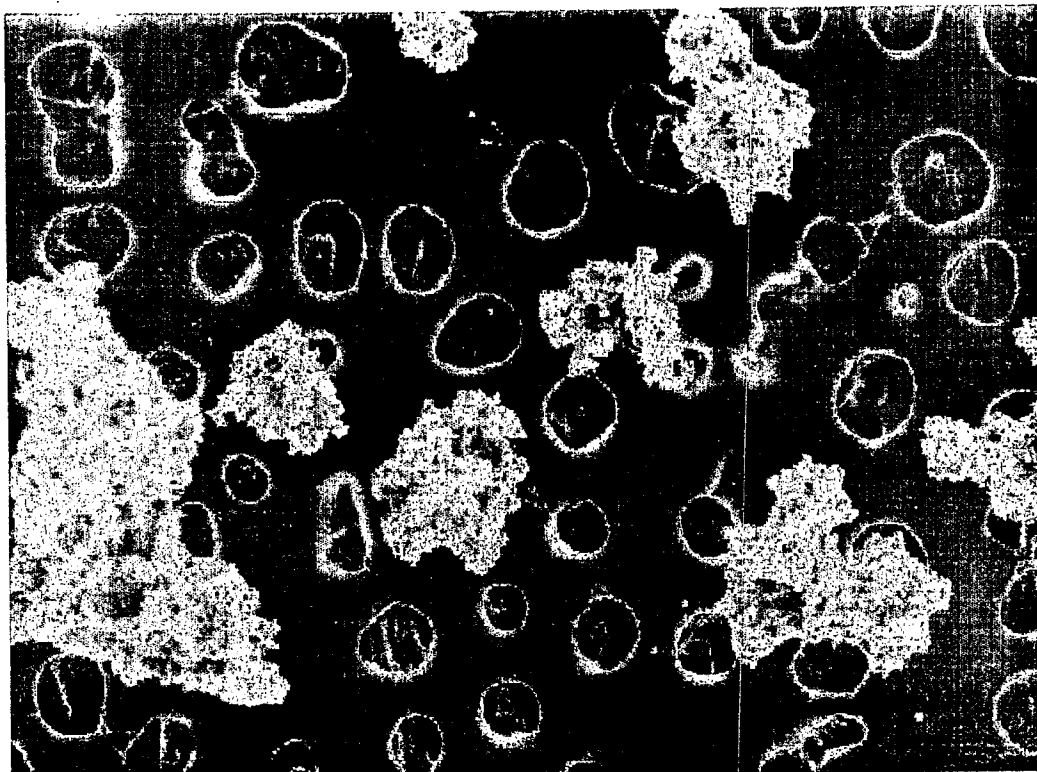


Width(μm): 2600.44 Height(μm): 1950.33 $\mu\text{m}/\text{pixel}$: 1.270
Scope magnification: 50X

FIGURE 1

2-8

File: NR286.02 50 mag Ti-B

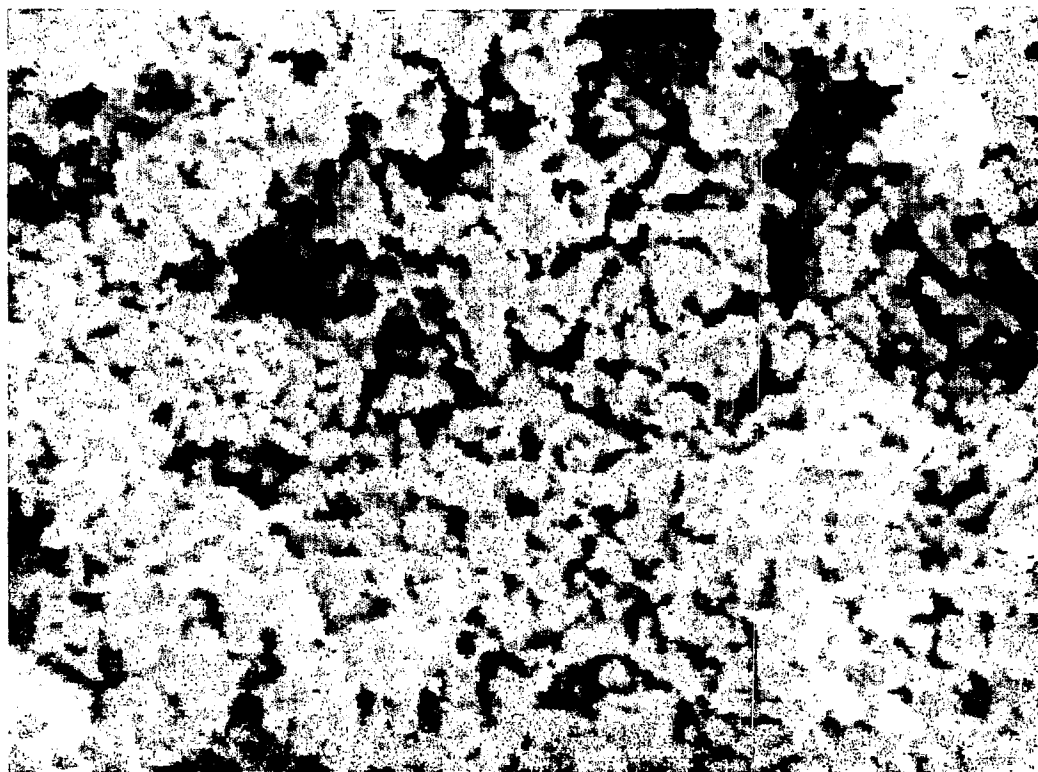
Width(μm): 2600.44Height(μm): 1950.33 $\mu\text{m}/\text{pixel}$: 2.539

Scope magnification: 50X

FIGURE 2

3-8

File: NR285.02 3000 mag Ti-B

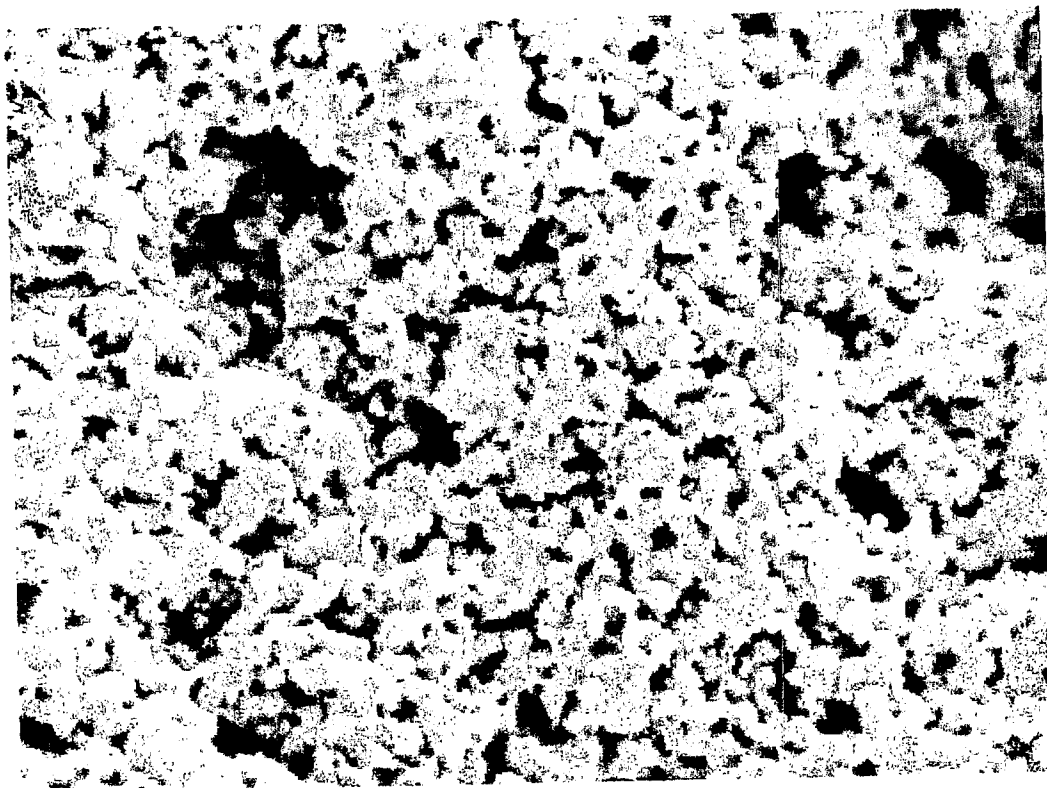


Width(μm): 48.00 Height(μm): 36.00 $\mu\text{m}/\text{pixel}$: 0.023
Scope magnification: 3000X

FIGURE 3

4-8

File: NR285.10 3000 mag Ti-B

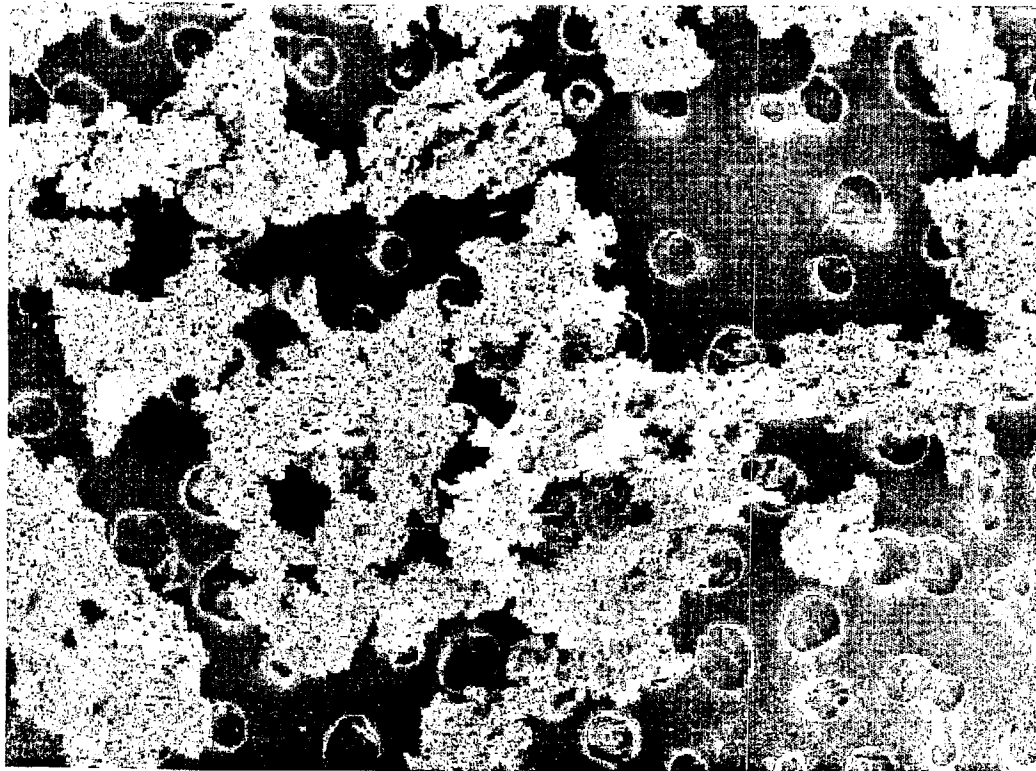


Width(μm): 48.00 Height(μm): 36.00 $\mu\text{m}/\text{pixel}$: 0.047
Scope magnification: 3000X

FIGURE 4

5-8

File: NR291 64B 40 mag agglomerates



Width(μm): 3164.83

Height(μm): 2373.63

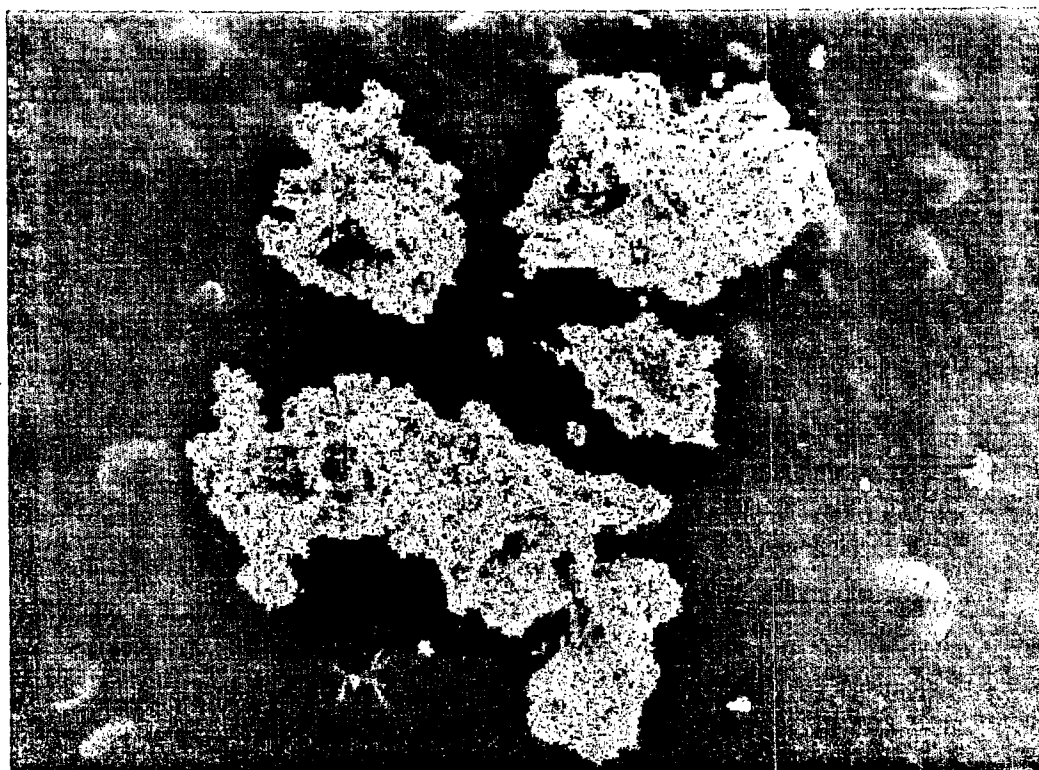
$\mu\text{m}/\text{pixel}$: 6.181

Scope magnification: 40X

FIGURE 5

6-8

File: NR292.01 50 mag 6/4 boron



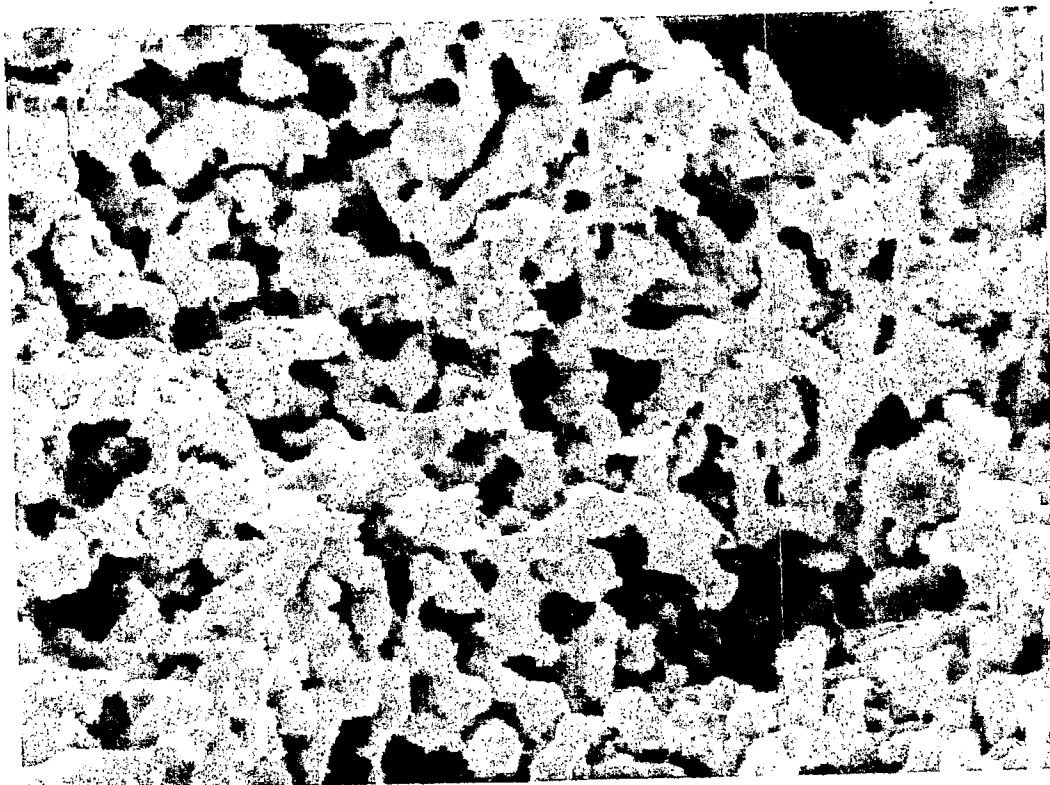
Width(μm): 2600.44 Height(μm): 1950.33 $\mu\text{m}/\text{pixel}$: 2.539

Scope magnification: 50X

FIGURE 6

7-8

File: NR291 3000 mag 64B

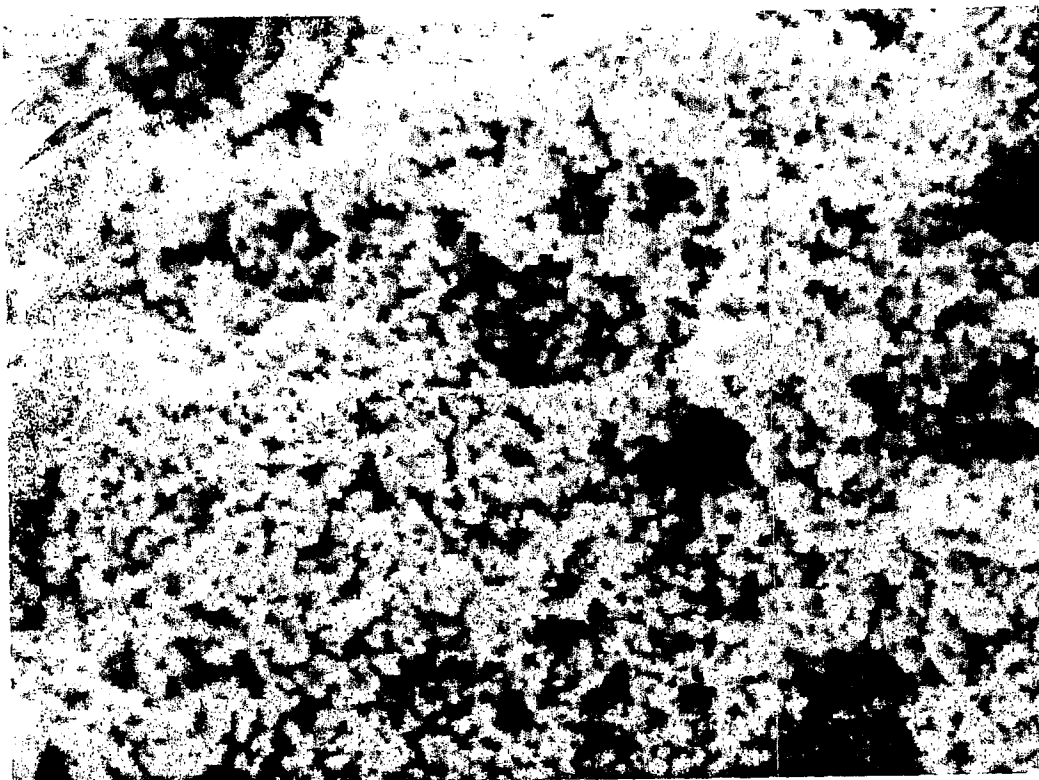


Width(μm): 48.00 Height(μm): 36.00 $\mu\text{m}/\text{pixel}$: 0.094
Scope magnification: 3000X

FIGURE 7

8-8

File: NR292.01 3000 mag 6/4 boron

Width(μm): 48.00Height(μm): 36.00 $\mu\text{m}/\text{pixel}$: 0.047

Scope magnification: 3000X

FIGURE 8

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 August 2007 (09.08.2007)

PCT

(10) International Publication Number
WO 2007/089400 A1

(51) International Patent Classification:
B22F 9/28 (2006.01) C22C 32/00 (2006.01)

(21) International Application Number:
PCT/US2007/000521

(22) International Filing Date: 9 January 2007 (09.01.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/346,123 2 February 2006 (02.02.2006) US

(71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **ARMSTRONG, Donn** [US/US]; W252 S 5000 Cartwright Cir., Waukesha, WI 53189 (US). **ANDERSON, Richard** [US/US]; 5836 Sunrise Avenue, Clarendon Hills, IL 60574 (US).

(74) Agent: **LEVY, Harry, M.; OLSON & HIERL LTD.,**
20 NORTH WACKER DRIVE, Suite 3600, Chicago, IL 60606 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

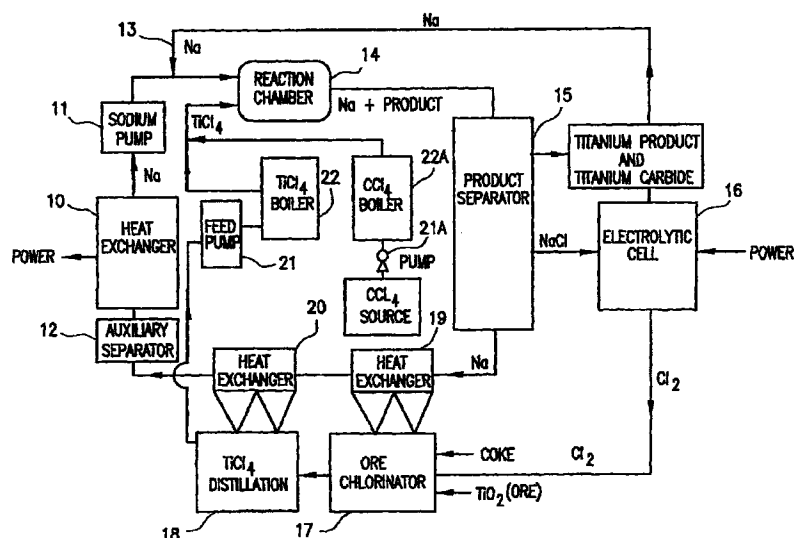
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METAL MATRIX WITH CERAMIC PARTICLES DISPERSED THEREIN



(57) Abstract: A metal matrix having ceramic particles distributed therein is made by the process of introducing a halide vapor of the metal forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof. A vapor of the constituents of the ceramic. Sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperatures to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal. The excess alkali and/or alkaline earth metal and the salt particles are removed leaving a mixture of metal matrix particles and ceramic particles. A method is also disclosed.

METAL MATRIX WITH CERAMIC PARTICLES DISPERSED THEREIN

FIELD OF THE INVENTION

This invention relates to compositions and methods of making same in which a metal matrix powder or particulates have distributed there through ceramic particles or particulates and solid objects made therefrom. The invention makes use of the Armstrong Process which is disclosed in U.S. patent nos. 6,409,797; 5,958,106; 5,779,761 and 6,861,038, all of the disclosures of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

Metallic matrices having ceramic particles distributed throughout are used in a significant number of industries. For instance, tungsten carbide is a very hard material and can be incorporated into various metal matrices to provide abrading materials, whereas titanium nitride and/or titanium carbides may be incorporated into a titanium matrix for use as cylinder liners in aluminum block engines.

In general, inorganic powder/particle manufacture has traditionally been made in a number of ways, comunion of solid metal, precipitation from a salt solution, thermal decomposition of a chemical compound, reduction of a compound, electrodeposition and the atomization of molten metals.

In general, atomization is used to produce spherical particles and brittle materials such as metal hydrides may be pulverized mechanically in ball mills and other known processes. Thermal decomposition of a chemical compound is used in some cases, such as nickel carbonyl. Some iron powders are also made this way.

With the advent of the Armstrong Process, the making of metal powders has been facilitated by the use of a liquid stream of alkali or alkaline earth metal into which is introduced a gaseous halide or a combination of halides under reducing conditions to make a metal or an alloy thereof, all as disclosed in the previously mentioned patents. The Armstrong Process can also be used to make ceramics, also set forth in above enumerated patents. Various commercial metals have been made with the Armstrong Process, most noticeably commercial pure (CP) titanium and 6/4 titanium meeting the ASTM grade 5 qualifications. However, there is a need

for compositions of metal or metal powder having ceramic particles or powder distributed throughout.

SUMMARY OF THE INVENTION

Accordingly, it is a principal object of the present invention to provide a composition of matter comprising a metal matrix having ceramic particles distributed therein made by the process of introducing a halide of the metal forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.

Another object of the present invention is to provide a composition of matter comprising a metal matrix having ceramic particles less than about one micron in average diameter distributed therein made by the process of introducing a chloride of the metal or metals forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and wherein the boiling points of the chlorides are less than about 500°C, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.

A final object of the invention is to provide a method of making a composition having a metal matrix powder with ceramic particles distributed therein, the method comprising establishing a stream of liquid alkali or alkaline earth metal or mixtures thereof, introducing halide vapor of the metal matrix and a source of a non-metal constituent of the ceramic particles at not less than sonic velocity into the liquid alkali or alkaline earth metal stream, the liquid alkali or alkaline earth metal being present

in sufficient quantity to maintain substantially all of the reaction products below the sintering temperatures thereof.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a process flow diagram showing the continuous process as an example titanium metal from titanium tetrachloride and a ceramic particulate mixed therewith; and

FIG. 2 is an example of a typical burner reaction chamber for the process disclosed in Figure 1.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention may be practiced with the use of any alkali or alkaline earth metal depending upon the metal or non-metal to be reduced. In some cases, combinations of an alkali or alkaline earth metals may be used. Moreover, any halide or combinations of halides may be used with the present invention although in most circumstances chlorine, being the cheapest and most readily available, is preferred. Of the alkali or alkaline earth metals, by way of example, sodium will be chosen not for purposes of limitation but merely purposes of illustration, because it is cheapest and preferred, as has chlorine been chosen for the same purpose, but magnesium is also commercially available.

Regarding the non-metals or metals to be reduced, it is possible to reduce a single metal such as titanium or tantalum or zirconium, selected from the list set forth hereafter. It is also possible to make alloys of a predetermined composition by providing mixed metal halides at the beginning of the process in the required

molecular ratio. By way of example, Table 1 sets forth heats of reaction per gram of liquid sodium for the reduction of a stoichiometric amount of a vapor of a non-metal or metal halides applicable to the inventive process.

TABLE 1

FEEDSTOCK	HEAT kJ/g
TiCl ₄	10
AlCl ₃	9
SiCl ₄	11
SnCl ₂	4
SbCl ₃	14
BeCl ₂	10
Bcl3	12
TaCl ₅	11
ZrCl ₄	9
VCl ₄	12
NbCl ₅	12
MoCl ₄	14
GaCl ₃	11
UF ₆	10
ReF ₆	17

Ceramic particles which are useful in the present invention may have a metal constituent selected from one or more of W, B, Bi, Fe, Gd, Ge, Hf, In, Pb, Sn, Zr, and these ceramics may be in the form of a nitride, a carbide, a phosphide, a sulfide, a boride or mixtures thereof.

It is best if the vapor introduced into the flowing metal stream has a boiling point of not greater than about 500°C, merely for purposes of using less expensive materials in the apparatus necessary to practice the invention. Sources of various materials useful in the present invention to provide ceramic particles are carbon

tetrachloride which has a boiling point of around 76.7°C; N₂; PCl₃ with a boiling point of about 76°C; SCl₂ with a boiling point of about 60°C; BCl₃ with a boiling point of about 13°C, where a halide is not useful for whatever reason, the element itself may be used in some cases, for instance, phosphorous sublimates at 417°C and sulfur boils at 445°C. Of course nitrogen is a gas at room temperature.

Various metallic components of ceramic parts such as for instance, tungsten tetrachloride with a boiling point of about 346°C may be used as well as other chlorides, fluorides or bromides, as is well known in the art. The compositions useful in the present invention depend on the end use thereof and the matrix may be as low as about 5% by weight or as high as 95% by weight, depending on the end use.

The process will be illustrated, again for purposes of illustration and not for limitation, with a single metal titanium being produced from the tetrachloride for the matrix material and TiC produced with CCl₄ for the ceramic.

A summary process flowsheet is shown in FIG. 1. Sodium and titanium tetrachloride are combined in a reaction chamber 14 where titanium tetrachloride vapor from a source thereof in the form of a boiler 22 is injected within a flowing sodium stream from a continuously cycling loop thereof including a sodium pump 11. Carbon tetrachloride from a source thereof is pumped by pump 21A to a boiler 22A and there to the line from boiler 22 to the reaction chamber 14. The sodium stream is replenished by sodium provided by an electrolytic cell 16. The reduction reaction in chamber 14 is highly exothermic, forming molten reaction products of titanium and sodium chloride with titanium carbide particles. Since TiC has a melting point in excess of 3000°, TiC particles when made are solid, not molten. The molten reaction products are quenched in the bulk sodium stream. Particle sizes and reaction rates are controlled by metering of the titanium tetrachloride vapor carbon tetrachloride flowrates (by controlling the supply pressure), dilution of the titanium tetrachloride vapor with an inert gas, such as He or Ar, and the sodium flow characteristics and mixing parameters in the reaction chamber which includes a nozzle for the titanium tetrachloride mixed with carbon tetrachloride and a surrounding conduit for the liquid sodium. The vapor is intimately mixed with the liquid in a zone enclosed by the liquid, i.e., a liquid continuum, and the resultant temperature, significantly affected by the heat of reaction, is controlled by the

quantity of flowing sodium and maintained below the sintering temperature of the produced metal, such as for titanium at about 1000 degree C. The ratio of Ti metal to TiC is controlled by flow controllers, not shown, providing adjustment of the gases flowing into reaction chamber 14. Preferably, the temperature of the sodium away from the location of halide introduction is maintained in the range of from about 200 degree C. to about 600 degree C. Products leaving the reaction zone are quenched in the surrounding liquid before contact with the walls of the reaction chamber and preferably before contact with other product particles. This precludes sintering and wall erosion.

The surrounding sodium stream then carries the titanium and titanium carbide and sodium chloride reaction products away from the reaction region. These reaction products are removed from the bulk sodium stream by conventional separators 15 such as cyclones, particulate filters, magnetic separators or vacuum stills, with vacuum distillation being preferred.

Three separate options for separation of the titanium and titanium carbide from the sodium chloride exist. The first option removes the titanium/titanium chloride and sodium chloride products in separate steps. This is accomplished by maintaining the bulk stream temperature such that the titanium/titanium carbide product is solid but the sodium chloride is molten through control of the ratio of titanium tetrachloride and sodium flowrates to the reaction chamber 14. For this option, the titanium/titanium carbide product is removed first, the bulk stream cooled to solidify the sodium chloride, then the sodium chloride is removed from separator 12.

In the second option for reaction product removal, a lower ratio of titanium tetrachloride to sodium flowrate would be maintained in the reaction chamber 14 so that the bulk sodium temperature would remain below the sodium chloride solidification temperature. For this option, titanium/titanium carbide product and sodium chloride would be removed simultaneously using conventional separators. The sodium chloride and any residual sodium present on the particles would then be removed in a water-alcohol wash.

In the third, and preferred option for product removal, the solid cake of salt, Ti/TiC product and Na is vacuum distilled to remove the Na. Thereafter, the Ti/TiC product is passivated by passing a gas containing some O₂ over the mixture of salt

and Ti/TiC product followed by a water wash to remove the salt leaving Ti/TiC product with surfaces of TiO_2 , which can be removed by conventional methods, if required.

Following separation, the sodium chloride is then recycled to the electrolytic cell 16 to be regenerated. The sodium is returned to the bulk process stream for introduction to reaction chamber 14 and the chlorine is used in the ore chlorination 17. It is important to note that while both electrolysis of sodium chloride and subsequent ore chlorination will be performed using technology well known in the art, such integration and recycle of the reaction by-product directly into the process is not possible with the Kroll or Hunter process because of the batch nature of those processes and the production of titanium sponge as an intermediate product. In addition, excess process heat is removed in heat exchanger 10 for co-generation of power. The integration of these separate processes enabled by the inventive chemical manufacturing process has significant benefits with respect to both improved economy of operation and substantially reduced environmental impact achieved by recycle of both energy and chemical waste streams.

Chlorine from the electrolytic cell 16 is used to chlorinate titanium ore (utile, agnates or ilmenite) in the chlorination 17. In the chlorination stage, the titanium ore is blended with coke and chemically converted in the presence of chlorine in a fluidized-bed or other suitable kiln chlorination. The titanium dioxide contained in the raw material reacts to form titanium tetrachloride, while the oxygen forms carbon dioxide with the coke. Iron and other impurity metals present in the ore are also converted during chlorination to their corresponding chlorides. The titanium chloride is then condensed and purified by means of distillation in column 18. With current practice, the purified titanium chloride vapor would be condensed again and sold to titanium manufacturers; however, in this integrated process, the titanium tetrachloride vapor stream is used directly in the manufacturing process via a feed pump 21 and boiler 22.

After providing process heat for the distillation step in heat exchangers 19 and 20, the temperature of the bulk process stream is adjusted to the desired temperature for the reaction chamber 14 at heat exchanger 10, and then combined with the regenerated sodium recycle stream, and injected into the reaction chamber.

The recovered heat from heat exchangers 19 and 20 may be used to vaporize liquid halides from the sources thereof to produce halide vapor to react with the metal or the non-metal. It should be understood that various pumps, filters, traps, monitors and the like will be added as needed by those skilled in the art.

In all aspects, for the process of FIG. 1, it is important that the titanium that is removed from the separator 15 be at or below the sintering temperature of titanium in order to preclude and prevent the solidification of the titanium on the surfaces of the equipment and the agglomeration of titanium particles into large masses, which is one of the fundamental difficulties with the commercial processes used presently. By maintaining the temperature of the titanium metal below the sintering temperature of titanium metal, the titanium will not attach to the walls of the equipment or itself as it occurs with prior art and, therefore, the physical removal of the same will be obviated. This is an important aspect of this invention and is obtained by the use of sufficient sodium metal or diluent gas or both to control the temperature of the elemental (or alloy) and ceramic product. In other aspects, FIG. 1, is illustrative of the types of design parameters which may be used to produce titanium particles/titanium carbide particles in a continuous process which avoids the problems with the prior art, and produces a more uniform distribution of ceramic particles.

Referring now to FIG. 2, there is disclosed a typical reaction chamber in which a choke flow or injection nozzle 23, completely submerged in a flowing liquid metal stream, introduces the halide vapors from boilers 22 and 22A in a controlled manner into the liquid metal reductant stream 13. The reaction process is controlled through the use of a choke-flow (sonic or critical flow) nozzle. A choke-flow nozzle is a vapor injection nozzle that achieves sonic velocity of the vapor at the nozzle throat. That is the velocity of the vapor is equal to the speed of sound in the vapor medium at the prevailing temperature and pressure of the vapor at the nozzle throat. When sonic conditions are achieved, any change in downstream conditions that causes a pressure change cannot propagate upstream to affect the discharge. The downstream pressure may then be reduced indefinitely without increasing or decreasing the discharge. Under choke flow conditions only the upstream conditions need to be controlled to control the flow-rate. The minimum upstream pressure

required for choke flow is proportioned to the downstream pressure and termed the critical pressure ratio. This ratio may be calculated by standard methods.

The choke flow nozzle serves two purposes: (1) it isolates the vapor generator from the liquid metal system, precluding the possibility of liquid metal backing up in the halide feed system and causing potentially dangerous contact with the liquid halide feedstock, and (2) it delivers the vapor at a fixed rate, independent of temperature and pressure fluctuations in the reaction zone, allowing easy and absolute control of the reaction kinetics.

The liquid metal stream also has multiple functional uses: (1) it rapidly chills the reaction products, forming product powder without sintering, (2) it transports the chilled reaction products to a separator, (3) it serves as a heat transfer medium allowing useful recovery of the considerable reaction heat, and (4) it feeds one of the reactants to the reaction zone.

For instance in FIG. 2, the sodium 13 entering the reaction chamber may be at 200.degree. C. having a flow rate of 38.4 kilograms per minute. The titanium tetrachloride from the boiler 22 may be at 2 atmospheres and at a temperature of 164.degree. C., the flow rate through the line may be 1.1 kg/min. Higher pressures may be used, but it is important that back flow be prevented, so the minimum pressure should be above that determined by the critical pressure ratio for sonic conditions, or about two times the absolute pressure of the sodium stream (two atmospheres if the sodium is at atmospheric pressure) is preferred to ensure that flow through the reaction chamber nozzle is critical or choked.

The subject process may also be used to provide a mixed powder of alloy and ceramic particles and to that end, the Armstrong Process has been used to make a 6/4 titanium alloy with ASTM definitions, that is 6% aluminum, 4% vanadium, the balance titanium and this alloy may also be produced by the Armstrong Process and have ceramic particles incorporated therein according to the present invention.

As has been stated before, the equipment used to produce the 6/4 alloy is substantially as disclosed in the aforementioned patents disclosing the Armstrong Process with the exception that instead of only having a titanium tetrachloride boiler 22 as illustrated in those patents, there is also a vanadium tetrachloride boiler and an aluminum trichloride boiler which are connected to the reaction chamber by suitable

valves. The piping acts as a manifold so that the gases are completely mixed as they enter the reaction chamber and are introduced subsurface to the flowing liquid sodium. It was determined during production of the 6/4 alloy that aluminum trichloride is corrosive and required special materials not required for handling either titanium tetrachloride or vanadium tetrachloride. Therefore, Hastelloy C-276 was used for the aluminum trichloride boiler and the piping to the reaction chamber.

During most of the runs the steady state temperature of the reactor was maintained at about 400°C by the use of sufficient excess sodium. Other operating conditions for the production of the alloy were as follows:

A device similar to that described in the incorporated Armstrong patents was used except that a VCl_4 boiler and AlCl_3 boiler were provided and both gases were fed into the line feeding TiCl_4 into the liquid Na. The boiler pressures and system parameters are listed hereafter.

Experimental Procedure:

TiCl_4 Boiler Pressure = 500 kPa

VCl_4 Boiler Pressure = 630 kPa

AlCl_3 Boiler Pressure = 830 kPa

Inlet Na temperature = 240°C

Reactor Outlet Temperature = 510 C

Na Flowrate = 40 kg/min

TiCl_4 Flowrate = 2.6 kg/min

For this specific experiment, a 7/32" nozzle was used in the reactor to meter the mix of metal chloride vapors. A .040" nozzle was used to meter the AlCl_3 and a .035" nozzle was used to meter the VCl_4 into the TiCl_4 stream. The reactor was operated for approximately 250 seconds injecting approximately 11 kg of TiCl_4 . The salt and titanium alloy solids were captured on a wedge wire filter and free sodium metal was drained away. The product cake containing titanium alloy, sodium chloride and sodium was distilled at approximately 100 milli - torr at 550 to 575°C vessel wall temperatures for 20 hours. Once all the sodium metal was removed via distillation, the trap was re-pressurized with argon gas and heated to 750°C and held at temperature for 48 hours. The vessel containing the salt and titanium alloy cake was cooled and the cake was passivated with a 0.7 wt % oxygen/argon mixture.

After passivation, the cake was washed with deionized water and subsequently dried in a vacuum oven at less than 100°C.

For instance, titanium carbide may be incorporated into a 6/4 alloy simply by including in the gas injected into the flowing sodium, a specified amount of carbon tetrachloride from boiler 22A, whereas a boride may be used by injecting into the flowing sodium, a specified amount of boron trichloride. Other ceramic particles may be produced from feed stocks as before described. As is seen, therefore, a wide variety of ceramic particles may be distributed in a metal matrix by using the Armstrong Process. Preferably, but not necessarily, the metal matrix incorporates at least one metal of the ceramic particle, but the invention is not so limited. The thermodynamics of the various reactions will determine what ceramic particles can be introduced into what matrix particles, but in general, the preferred ceramics are nitrides, phosphide, sulfides and carbides. Oxides are not preferred with titanium as the oxide would react with the titanium.

After the powder is made, a wide variety of processes may be used to make solid articles therefrom and these processes are widely known and commonly used in the powder metallurgy art and include casting, press and sinter and well as many others including arc melting and the like.

While the invention has been particularly shown and described with reference to a preferred embodiment hereof, it will be understood by those skilled in the art that several changes in form and detail may be made without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A composition of matter comprising a metal matrix having ceramic particles distributed therein made by the process of introducing a halide of the metal forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.
2. The composition of matter of claim 1, wherein the boiling point of the halides is less than about 500°C.
3. The composition of matter of claim 1, wherein said metal matrix is one or more of Ti, Al, Sb, Be, B, Ta, V, Nb, Mo, Ga, U, Re, Zr, Si, and alloys thereof.
4. The composition of matter of claim 1, wherein said ceramic particles have a metal constituent selected from W, B, Bi, Cr, Fe, Gd, Ge, Hf, In, Pb, Sn, Zr, and mixtures or alloys thereof.
5. The composition of matter of claim 1, wherein said ceramic is a nitride, a carbide, a phosphide, a sulfide, a boride or mixtures thereof.
6. The composition of matter of claim 1, wherein said halide is a chloride.
7. The composition of matter of claim 1, wherein said metal matrix is Ti or an alloy thereof.
8. The composition of matter of claim 7, wherein said metal matrix is an aluminum and vanadium alloy of titanium.
9. The composition of matter of claim 1, wherein said halide is introduced into said flowing metal at greater than sonic velocity.
10. The composition of matter of claim 1, wherein said flowing metal is Na or Mg.
11. A solid article made from the composition of matter of claim 1.
12. A composition of matter comprising a metal matrix having ceramic particles less than about one micron in average diameter distributed therein made by

the process of introducing a chloride of the metal or metals forming the matrix into flowing alkali or alkaline earth metal or mixtures thereof, introducing a source of the constituents of the ceramic into flowing alkali or alkaline earth metal or mixtures thereof, wherein sufficient excess alkali and/or alkaline earth metal is present to maintain the temperature of substantially all of the reaction products below the sintering temperature thereof to produce metal matrix particles and ceramic particles and salt particles in excess alkali and/or alkaline earth metal, and wherein the boiling points of the chlorides are less than about 500°C, and removing the excess alkali and/or alkaline earth metal and the salt particles leaving a mixture of metal matrix particles and ceramic particles.

13. The composition of matter of claim 12, wherein said metal matrix is one or more of Ti, Al, Sb, Be, B, Ta, V, Nb, Mo, Ga, U, Re, Zr, Si, and alloys thereof.

14. The composition of matter of claim 13, wherein said ceramic is a nitride, a carbide, a phosphide, a sulfide, a boride or mixtures thereof.

15. The composition of matter of claim 14, wherein said ceramic particles have a metal constituent selected from W, B, Bi, Cr, Fe, Gd, Ge, Hf, In, Pb, Pt, Sn, Zr, and mixtures or alloys thereof.

16. The composition of matter of claim 15, wherein said metal matrix is Ti or an alloy thereof.

17. The composition of matter of claim 16, wherein said ceramic particles include a carbide and/or a nitride.

18. The composition of matter of claim 16, wherein said ceramic particles include a boride.

19. The composition of matter of claim 12, wherein the metal constituent of the ceramic is the same as said metal matrix.

20. A solid article made from the composition of matter of claim 12.

21. A method of making a composition having a metal matrix powder with ceramic particles distributed therein, said method comprising establishing a stream of liquid alkali or alkaline earth metal or mixtures thereof, introducing halide vapor of the metal matrix and a source of a non-metal constituent of the ceramic particles at not less than sonic velocity into the liquid alkali or alkaline earth metal stream, the liquid alkali or alkaline earth metal being present in sufficient quantity to maintain

substantially all of the reaction products below the sintering temperatures thereof.

22. The method of claim 21, and further comprising forming the composition of powder into a solid article.

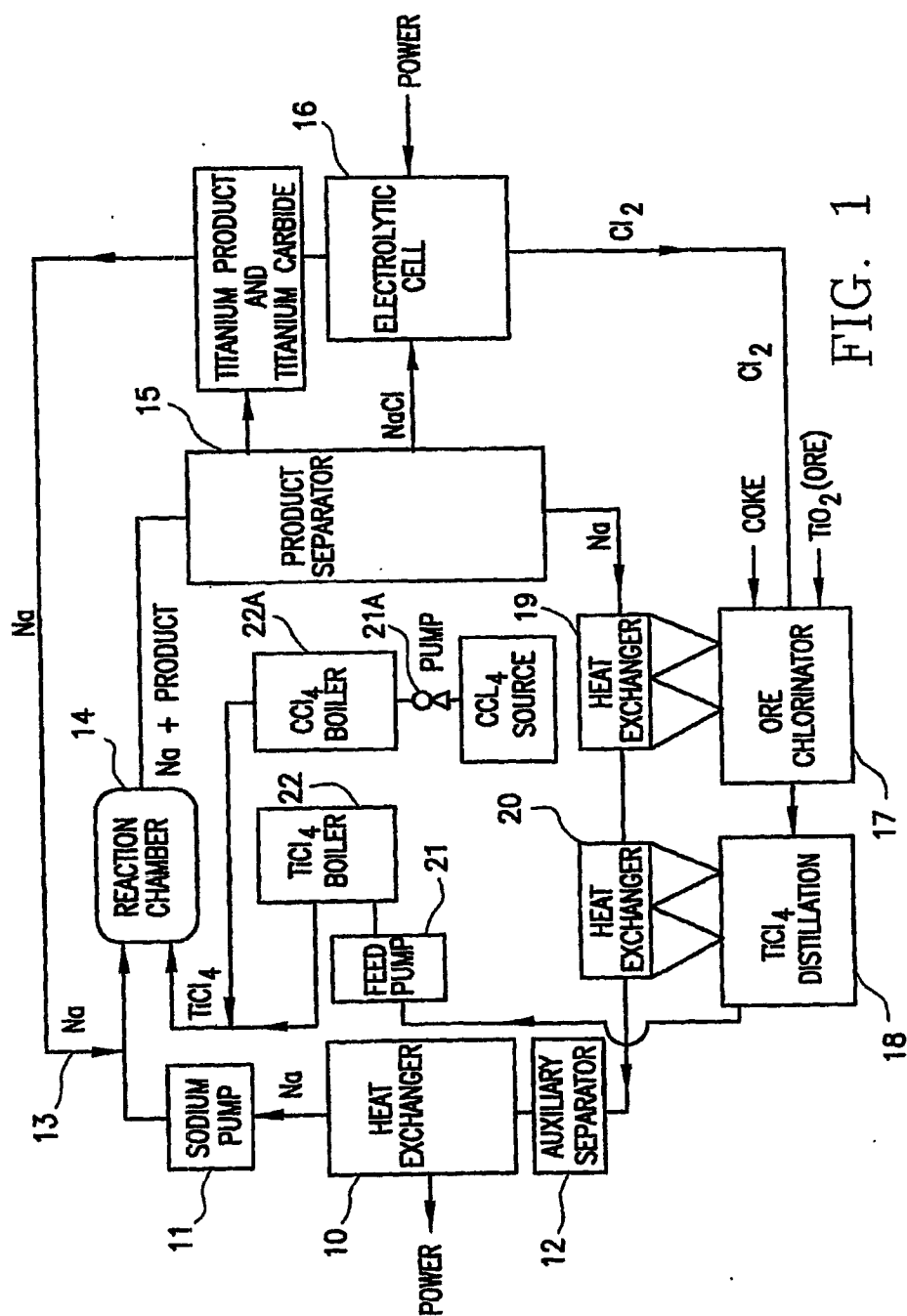


FIG. 1

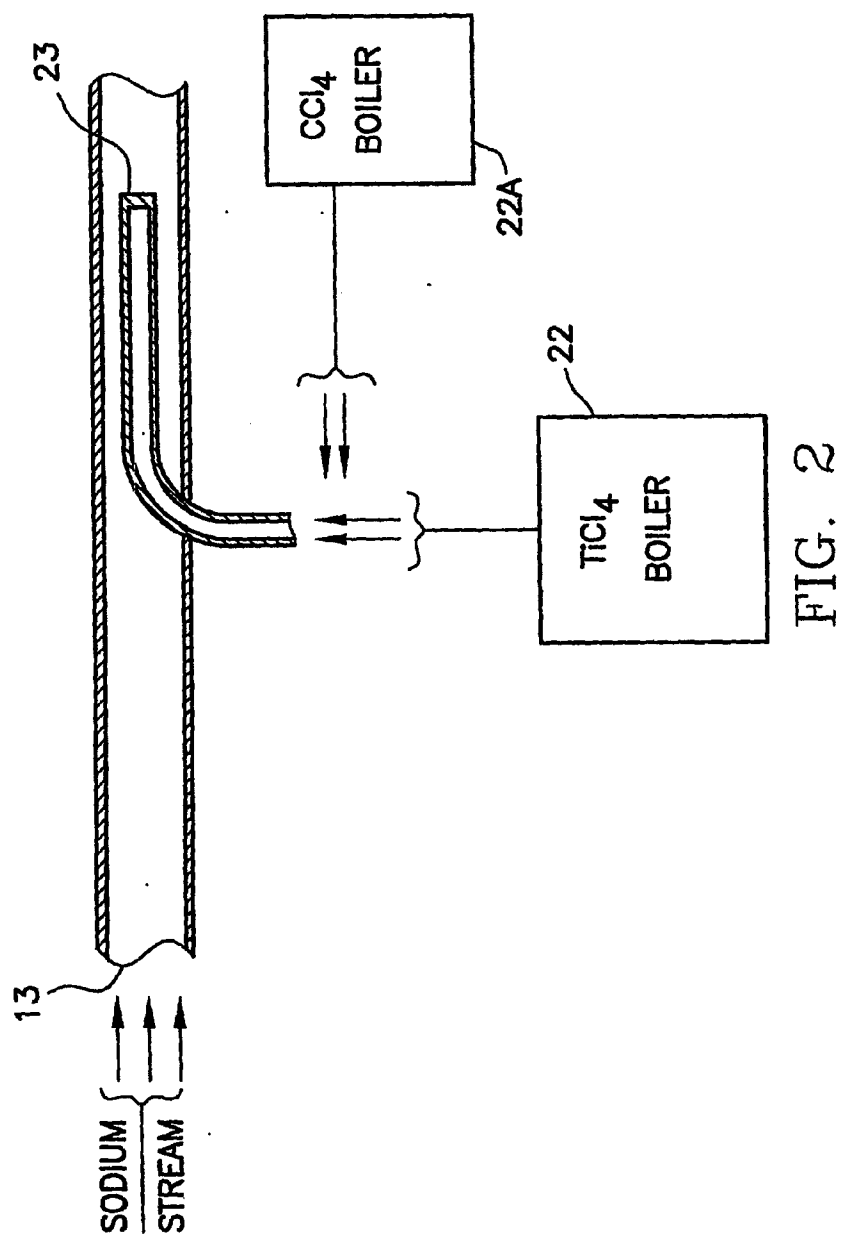


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/000521

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F9/28 C22C32/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 441 039 A (GEN ELECTRIC [US]) 28 July 2004 (2004-07-28) column 5, line 11 - line 13 column 6, line 45 - line 46 paragraph [0023] - paragraph [0025] figure 3	1-22
X	WO 98/24575 A (DYNAMET TECHNOLOGY [US]) 11 June 1998 (1998-06-11) abstract	1,3-5,7, 8,11, 13-20
X	JP 05 078762 A (SUMITOMO LIGHT METAL IND) 30 March 1993 (1993-03-30) abstract	1,3-5,7, 11,13-20
	----- -/-- -----	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

15 May 2007

Date of mailing of the international search report

25/05/2007

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Morra, Valentina

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2007/000521

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 958 106 A (ARMSTRONG DONN REYNOLDS [US] ET AL) 28 September 1999 (1999-09-28) cited in the application the whole document -----	1,2
A	WO 2004/022797 A1 (INTERNAT TITANIUM POWDER LLC [US]; ANDERSON RICHARD [US]; ARMSTRONG DO) 18 March 2004 (2004-03-18) the whole document -----	1-22
X,E	WO 2007/044635 A (INTERNAT TITANIUM POWDER LLC [US]; JACOBSEN LANCE [US]; BENISH ADAM JO) 19 April 2007 (2007-04-19) the whole document -----	1-16, 18-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/000521

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1441039	A	28-07-2004	US 2004141869 A1	22-07-2004
WO 9824575	A	11-06-1998	US 5897830 A	27-04-1999
JP 5078762	A	30-03-1993	NONE	
US 5958106	A	28-09-1999	NONE	
WO 2004022797	A1	18-03-2004	AU 2003263047 A1	29-03-2004
			CA 2500909 A1	18-03-2004
			CN 1688731 A	26-10-2005
			JP 2005538251 T	15-12-2005
WO 2007044635	A	19-04-2007	NONE	

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 January 2008 (31.01.2008)

PCT

(10) International Publication Number
WO 2008/013518 A1

(51) International Patent Classification:

C22B 34/12 (2006.01) C22C 14/00 (2006.01)
C22C 1/04 (2006.01)

(21) International Application Number:

PCT/US2006/028396

(22) International Filing Date: 22 July 2006 (22.07.2006)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US): **INTERNATIONAL TITANIUM POWDER, LLC.** [US/US];
20634 W. Gaskin Drive, Lockport, IL 60441 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JACOBSEN, Lance**
[US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).
BENSIH, Adam, John [US/US]; 1918 Highland Avenue,
Crest Hill, IL 60435 (US).

(74) Agent: **LEVY, Harry, M.**; Emrich and Dithmar, LLC.,
125 South Wacker Drive, Suite 2080, Chicago, IL 60606
(US).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP,
KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT,
LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA,
NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC,
SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ,
UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- the filing date of the international application is within two
months from the date of expiration of the priority period
- with information concerning one or more priority claims
considered void

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: TITANIUM ALLOY

(57) Abstract: A titanium base alloy powder having lesser amounts of aluminum and vanadium with an alkali or alkaline earth metal being present in an amount of less than about 200 ppm. The alloy powder is neither spherical nor angular and flake shaped. 6/4 alloy is specifically disclosed having a packing fraction or tap density between 4 and 11 %, as is a method for making the various alloys.



WO 2008/013518 A1

TITANIUM ALLOY

FIELD OF THE INVENTION

This invention relates to alloys of titanium having at least 50% titanium and most specifically to an alloy of titanium particularly useful in the aerospace and defense industries known as 6/4 which is about 6% by weight aluminum and about 4% by weight vanadium with the balance titanium and trace materials as made by the Armstrong process.

BACKGROUND OF THE INVENTION

The ASTM B265 grade 5 chemical specifications for 6/4 require that vanadium is present in the amount of 4% \pm 1% by weight and aluminum is present in the range of from about 5.5 % to about 6.75 % by weight. The alloy of the invention is produced by the Armstrong Process as previously disclosed in U.S. patent nos. 5,779,761; 5,958,106 and 6,609,797, the entire disclosures of which are herein incorporated by reference. The aforementioned patents teach the Armstrong Process as it relates to the production of various materials including alloys. The Armstrong Process includes the subsurface reduction of halides by a molten metal alkali or alkaline earth element or alloy. The development of the Armstrong Process has occurred from 1994 through the present, particularly as it relates to the production of titanium and its alloys using titanium tetrachloride as a source of titanium and using sodium as the reducing agent. Although this invention is described particularly with respect to titanium tetrachloride, aluminum trichloride and vanadium tetrachloride and sodium as a reducing metal, it should be understood that various halides other than chlorine can be used and various reductants other than sodium can be used and the invention is broad enough to include those materials.

However, because the Armstrong Process over the past eleven years has been developed using molten sodium and chlorides, it is these materials which are referenced herein. During the production of titanium by the Armstrong Process, as disclosed in the previous patents, the steady state temperature of the reaction can be controlled by the amount of reductant metal and the amount of chloride being introduced. Although it is feasible to control the reaction temperature by varying the chloride concentration while keeping the amount of molten metal constant, the

preferred method is to control the temperature of the reactant products by varying the amount of excess (over stoichiometric) reductant metal introduced into the reaction chamber. Preferably, the reaction is maintained at a steady state temperature of about 400°C and at this temperature, as previously disclosed, the reaction can be maintained for very long periods of time without damage to the equipment while producing a relatively uniform product.

Heretofore, commercially pure (CP) titanium ASTM B265 grades 1, 2, 3 and 4 have been produced in over two hundred runs using the Armstrong Process and although a wide variety of operating parameters have been tested, certain results are inherent in the process. The ASTM B 265 spec sheet follows:

TABLE 1 - Chemical Requirements

Element	Composition %									
	Grade									
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Nitrogen max	0.03	0.03	0.05	0.05	0.05	0.05	0.03	0.02	0.03	0.03
Carbon max	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.08
Hydrogen ^b max	0.015	0.015	0.015	0.015	0.015	0.020	0.015	0.015	0.015	0.015
Iron Max ^c	0.20	0.30	0.30	0.50	0.40	0.50	0.30	0.25	0.20	0.30
Oxygen max	0.18	0.25	0.35	0.40	0.20	0.20	0.25	0.15	0.18	0.25
Aluminum	5.5 to 6.75	4.0 to 6.0	...	2.5 to 3.5
Vanadium	3.5 to 4.5	2.0 to 3.0	...
Tin	2.0 to 3.0
Palladium	0.12 to 0.25	...	0.12 to 0.25	...
Molybdenum	0.2 to 0.4
Zirconium
Nickel	0.6 to 0.9
Residuals ^{c,d,e}	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
(each), max										
Residuals ^{c,d,e}	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
(total) max										
Titanium ^f	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder	remainder

^a Analysis shall be completed for all elements listed in this Table for each grade. The analysis results for the elements not quantified in the Table need not be reported unless the concentration level is greater than 0.1% each or 0.4% total.

^b Lower hydrogen may be obtained by negotiation with the manufacturer.

^c Need not be reported.

^d A residual is an element present in a metal or an alloy in small quantities inherent to the manufacturing process but not added intentionally.

^e The purchaser may, in his written purchase order, request analysis for specific residual elements not listed in this specification. The maximum allowable concentration for residual elements shall be 0.1% each and 0.4% maximum total.

^f The percentage of titanium is determined by difference.

Production of titanium powder by the Armstrong Process inherently produces powder in which the average diameter of an individual particle is less than a micron. During distillation at 500 to 600°C, the particles agglomerate and have an average agglomerated particle diameter in the range of from about 3.3 to about 1.3 microns. Particle diameters are based on a calculated size of a sphere from a surface area, such as BET. For agglomerated particles, the calculated average diameters were based on surface area measurements in a range of from about 0.4 to about 1.0 m² per gram. In over two hundred runs, the titanium powder produced by the Armstrong Process always has a packing fraction in the range of from about 4% to about 11% which also may also be expressed as tap density. Tap density is a well known characteristic and is determined by introducing the powder into a graduated test tube and tapping the tube until the powder is fully settled. Thereafter, the weight of the powder is measured and the packing fraction or percent of theoretical density is calculated.

Moreover, during the production of CP titanium by the Armstrong Process, a certain amount of sodium has always been retained even after extensive distillation, including vacuum distillation, and this retained sodium has been present on average of about 500 - 700 ppm, and has rarely been below about 400 ppm. From a commercial point of view, significant effort is and has been expended in order to reduce the sodium content of CP titanium made by the Armstrong Process.

Prior to the Armstrong Process, CP titanium powder and titanium alloy powder traditionally have been made by two methods, hydride-dehydride and spheridization, resulting in powders having very different morphologies than the powder made by the Armstrong method. Hydride-dehydride powders are angular and flake-like, while spheridized powders are spheres.

Fines made during the Hunter process are available and these also have very different morphology than CP titanium produced by the Armstrong Process. SEMs of CP powder made by the hydride-dehydride process and the spheridization process and Hunter fines are illustrated in Figs. 1 to 3, respectively. The CP powder made by the Armstrong Process is not spherical nor is it angular and flake-like. Hunter fines have "large inclusions" which do not appear in the Armstrong powder, differentiating Figs. 1-3 from Armstrong powder shown in Figs. 4 - 9. Moreover, Hunter fines have

large concentrations of chlorine while Armstrong CP powder has low concentrations of chlorine; chlorine is an undesirable contaminant.

6/4 powder is made by hydride-dehydride and spherization processes, but not by the Hunter process. A calcium reduction hydride-dehydride process used in Tula, Russia was identified by Moxson et al. in an article in The International Journal Of Powder Metallurgy, Vol. 34, No. 5, 1998. Moxson et al which also discloses SEMs of both CP and 6/4 in the Journal Of Metallurgy, May, 2000, both articles, the disclosures of which are incorporated by reference, taken together showing that 6/4 powder made by methods other than the Armstrong process result in powders that are very different from Armstrong 6/4 powder, both in size distribution and/or morphology and/or chemistry. In some cases, such as the calcium reduction process in Tula, Russia there are very significant differences in chemistry as well as the other differences previously mentioned. Both the hydride -dehydride and spheridization methods require Ti, Al and V to be mixed as liquids and thereafter formed into powder. Only the Armstrong Process produces alloy powder directly from gas mixtures of the alloy constituents.

Because 6/4 titanium is the most common titanium alloy used by the Department of Defense (DOD) as well as the aerospace industry and other significant industries, the production of 6/4 by the Armstrong Process is an important commercial goal.

SUMMARY OF THE INVENTION

Accordingly, a principal object of the present invention is to provide a titanium base alloy powder having lesser amounts of aluminum and vanadium with unique morphological and chemical properties.

Another object of the present invention to provide a titanium base alloy powder having about 6 percent by weight aluminum and about 4 percent by weight vanadium within current ASTM specifications.

Yet another object of the invention is to make a 6/4 alloy as set forth in which sodium is present in significantly smaller amounts than is present in CP titanium powder made by the Armstrong Process.

Still another object of the present invention is to provide a titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with

an alkali or alkaline earth metal being present in an amount less than about 200 ppm and the alloy powder being neither spherical nor angular or flake shaped.

A further object of the present invention is to provide a titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 200 ppm and having a tap density or packing fraction in the range of from about 4% to about 11%.

Yet another object of the present invention is to provide a titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or an alkaline earth metal being present in an amount less than about 200 ppm made by the subsurface reduction of chloride vapor with molten alkali metal or molten alkaline earth metal.

A final object of the present invention is to provide an agglomerated titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 100 ppm substantially as seen in the SEMs of Figs. 10-12.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURE 1 is a SEM of CP powder made by the hydride-dehydride method;

FIG. 2 is a SEM of CP powder made by the spheridization method;

FIG. 3 is a SEM of CP powder from the Hunter Process;

FIGS. 4-6 are SEMs of Armstrong CP distilled, dried and passivated;

FIGS. 7-9 are SEMs of Armstrong CP distilled, dried, passivated and held at

750°C for 48 hours; and

FIGS. 10-12 are SEMs of Armstrong 6/4 distilled, dried, passivated and held at 750°C for 48 hours.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, a "titanium base alloy" means any alloy having 50% or more by weight titanium. Although 6/4 is used as a specific example, other titanium base alloys are included in this invention. As seen from the previous discussion, Armstrong CP titanium powder is different from spheridized titanium powder and from hydride-dehydride titanium powder in both morphology and packing fraction or tap density. There are also differences in certain of the chemical constituents. For instance, Armstrong CP titanium powder has sodium present in the 400 - 700 ppm range while spheridized and hydride-dehydride powder should have none or only trace amounts. Armstrong CP titanium has little chloride concentration, on the order of <50 ppm, while Hunter fines have much larger concentrations of chlorides, on the order of 0.12 - 0.15 wt. %.

The equipment used to produce the 6/4 alloy is substantially as disclosed in the aforementioned patents disclosing the Armstrong Process with the exception that instead of only having a titanium tetrachloride boiler 22 as illustrated in those patents, there is also a vanadium tetrachloride boiler and an aluminum trichloride boiler which are connected to the reaction chamber by suitable valves. The piping acts as a manifold so that the gases are completely mixed as they enter the reaction chamber and are introduced subsurface to the flowing liquid sodium. It was determined during production of the 6/4 alloy that aluminum trichloride is corrosive and required special materials not required for handling either titanium tetrachloride or vanadium tetrachloride. Therefore, Hastelloy C-276 was used for the aluminum trichloride boiler and the piping to the reaction chamber.

During most of the runs the steady state temperature of the reactor was maintained at about 400°C by the use of sufficient excess sodium. Other operating conditions for the production of the alloy were as follows:

A device similar to that described in the incorporated Armstrong patents was used except that a VCl_4 boiler and AlCl_3 boiler were provided and both gases were fed into the line feeding TiCl_4 into the liquid Na. The boiler pressures and system

parameters are listed hereafter.

Experimental Procedure:

TiCl₄ Boiler Pressure = 500 kPa

VCl₄ Boiler Pressure = 630 kPa

AlCl₃ Boiler Pressure = 830 kPa

Inlet Na temperature = 240°C

Reactor Outlet Temperature = 510 C

Na Flowrate = 40 kg/min

TiCl₄ Flowrate = 2.6 kg/min

For this specific experiment, a 7/32" nozzle was used in the reactor to meter the mix of metal chloride vapors. A .040" nozzle was used to meter the AlCl₃ and a .035" nozzle was used to meter the VCl₄ into the TiCl₄ stream. The reactor was operated for approximately 250 seconds injecting approximately 11 kg of TiCl₄. The salt and titanium alloy solids were captured on a wedge wire filter and free sodium metal was drained away. The product cake containing titanium alloy, sodium chloride and sodium was distilled at approximately 100 milli - torr at 550 to 575°C vessel wall temperatures for 20 hours. Once all the sodium metal was removed via distillation, the trap was re-pressurized with argon gas and heated to 750°C and held at temperature for 48 hours. The vessel containing the salt and titanium alloy cake was cooled and the cake was passivated with a 0.7 wt % oxygen/argon mixture. After passivation, the cake was washed with deionized water and subsequently dried in a vacuum oven at less than 100°C.

Table 1 below sets forth a chemical analysis of various runs for 6/4 alloy from an experimental loop running the Armstrong Process.

TABLE 2
Ti 6/4 FROM EXPERIMENTAL LOOP

<u>Run</u>	<u>Size</u>	<u>Oxygen</u>	<u>Sodium</u>	<u>Nitrogen</u>	<u>Hydrogen</u>	<u>Chloride</u>	<u>Vanadium</u>	<u>Aluminum</u>	<u>Carbon</u>	<u>Iron</u>
N-269-	*	0.187	0.019	0.006	0.0029	0.001	5.58	5.58	0.019	0.014
N-269-	+	0.113	0.0015	0.008	0.003	0.001	5.33	5.38	0.03	0.021
N-269-	+	0.128	0.0006	0.005	0.0037	0.001		5.84	5.47	0.039
N-271-	+	0.124	0.002	0.001	0.0066	0.0016	4.87	6.95	0.033	0.037
N-276	+	0.111	0.0018					4.44	6.04	
N-276	+	0.121	0.0018	0.005	0.0043	0.0005		4.12	6.35	0.012
N-276	+	0.131	0.0019	0.003	0.0057	0.0011		4.03	5.67	0.012
N-276	+	0.169	0.0026					4.1	6.02	
N-276	+	0.128	0.0015	0.003	0.0042	0.0005		3.8	6.02	0.012
N-277	+	0.155	0.0018	0.003	0.0053	0.0006		3.45	5.73	0.014
N-277	+	0.135	0.0023					3.49	5.49	
N-276	*	0.121	0.0041	0.005	0.0052	0.0005		4.31	6.53	0.02
N-276	*	0.134	0.0075					3.81	5.92	
N-276	*	0.175	0.014	0.012	0.0066	0.0005			3.96	6.01
N-276	*	0.187	0.046	0.007	0.0081	0.0005			3.95	6.05
N-277	*	0.141	0.0022	0.004	0.0038	0.0026		3.65	5.42	
mean		0.14125	0.0069125	0.0051667	0.00495	0.00095	4.295625	5.914375	0.0212222	0.0192222
stand dev.		0.0253811	0.0116064	0.0028868	0.0015952	0.000626	0.7343838	0.4335892	0.0102808	0.0071024

* = BULK

+ = SMALL

As seen from the above Table 2, the sodium levels for 6/4 are very low on the order of 69 ppm and for certain runs, sodium levels have been undetectable. This result was unexpected because over two hundred runs of CP titanium have been made using the Armstrong Process, and sodium has always been present in the range of from about 400-700 ppm. Therefore, the lack of sodium in the 6/4 alloy was not only unexpected but an important consideration since sodium may adversely affect the welds of CP titanium.

Other important aspects shown in Table 2 are the percentages of vanadium and aluminum in the 6/4 showing an average of about 5.91% aluminum and about 4.29% vanadium for all of the runs. The runs reported in Table 2 were made with an experimental loop and the valving and control systems for metering the appropriate amount of both vanadium and aluminum were rudimentary. Advanced valving systems have now been installed to control more closely the amount of vanadium and aluminum in the 6/4 produced from the Armstrong Process, although even with the rudimentary control system, the 6/4 alloy was within ASTM specifications. Also of significance is the low iron and chloride content of the 6/4 alloy.

An additional unexpected feature of the 6/4 alloy compared to the CP titanium is the surface area, as determined using BET Specific Surface Area analysis with krypton as the adsorbate. In general, the specific surface area of the 6/4 alloy is much larger than the CP titanium and this also was unexpected. Surface analysis of CP particles which were distilled overnight (about 8-12 hours) between 500 - 575°C were 0.534 square meters/gram whereas 6/4 alloy measured 3.12 square meters/gram, indicating that the alloy is significantly smaller than the CP.

The SEMs show that the 6/4 powder is "frillier" than CP powder, see Figs. 4-9 and 10-12. As reported by Moxson et al., *Innovations in Titanium Powder Processing* in the

Journal of Metallurgy May 2000, it is clear that by-product fines from the Kroll or Hunter Processes contain large amounts of undesirable chlorine which is not present in the CP titanium powder made by the Armstrong Process (see Table 1). Moreover, the morphology of the Hunter and Kroll fines, as previously discussed, is different from the CP powder made by the Armstrong Process. Neither the Kroll nor the Hunter process has been adapted to produce 6/4 alloy. Alloy powders have been produced by melting prealloyed stock and thereafter using either gas atomization or a hydride-dehydride process (MHR). The Moxson et al. article discloses 6/4 powder made in Tula, Russia and as seen from Fig. 2 in that article, particularly Figures 2c and 2d the powders made by Tula Hydride Reduction process are significantly different than those made by the Armstrong Process. Moreover, referring to the Moxson et al. article in the 1998 issue of the International Journal of Powder Metallurgy, Vol. 4, No. 5, pages 45-47, it is seen that the chemical analysis for the pre-alloy 6/4 powder produced by the metal-hydride reduction (MHD) process contains exceptional amounts of calcium and also is not within ASTM specifications for aluminum.

Because the 6/4 alloy made by the Armstrong Process is made without the presence of either calcium or magnesium, these metals should be present, if at all, only in trace amounts and certainly much less than 100 ppm. Sodium which would be expected to be present in significant quantities based on the operation of the Armstrong Process to produce CP titanium in fact is present only at minium quantities in the 6/4 alloy. Specifically, sodium in the 6/4 alloy made by the Armstrong Process is almost always present less than 200 ppm and generally less than 100 ppm. In some instances, 6/4 alloy has been produced using the Armstrong Process in which sodium is undetectable so that this is a great and unexpected advantage of the 6/4 alloy *vis a vis* CP titanium made by

the Armstrong Process.

Both the Armstrong CP titanium and 6/4 alloy have tap densities or packing fractions in the range of from about 4% to 11%. This tap density or packing fraction is unique and inherent in the Armstrong Process and, while not advantageous particularly with respect to powder metallurgical processing, distinguishes the CP powder and the 6/4 powder made by the Armstrong Process from all other known powders.

As is well known in the art, solid objects can be made by forming 6/4 or CP titanium into a near net shapes and thereafter sintering, see the Moxson et al. article and can also be formed by hot isostatic pressing, laser deposition, metal injecting molding, direct powder rolling or various other well known techniques. Therefore, the titanium alloy powder made by the Armstrong method may be formed into a sintered product or may be formed into a solid object by well known methods in the art and the subject invention is intended to cover all such products made from the powder of the subject invention.

While the invention has been particularly shown and described with reference to a preferred embodiment hereof, it will be understood by those skilled in the art that several changes in form and detail may be made without departing from the spirit and scope of the invention which includes titanium base alloys having lesser amounts of aluminum and vanadium and is specifically not limited to the specific alloys disclosed.

WE CLAIM:

1. A titanium base alloy powder having lesser amounts of aluminum and vanadium with an alkali or alkaline earth metal being present in an amount of less than about 200 ppm and said alloy powder being neither spherical nor angular and flake shaped.
2. The titanium base alloy of claim 1, wherein the total amount of aluminum and vanadium is less than about 20% by weight.
3. The titanium alloy powder of claim 1, wherein said powder is in agglomerates having an average mean diameter as measured by sieve analysis greater than about 50 microns.
4. The titanium alloy powder of claim 1, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.
5. The titanium alloy powder of claim 1, wherein sodium and magnesium and calcium are present in an amount of less than about 100 ppm.
6. The titanium alloy powder of claim 1, wherein the tap density is in the range of from about 4% to about 11%.
7. The titanium alloy powder of claim 1 formed into a sintered product.
8. A solid object made from the titanium alloy powder of claim 1.
9. A titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount of less than about 200 ppm and said alloy powder being neither spherical nor angular and flake shaped.

10. The titanium alloy powder of claim 9, wherein said powder is in agglomerates having an average mean diameter as measured by sieve analysis greater than about 50 microns.

11. The titanium alloy powder of claim 9, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

12. The titanium alloy powder of claim 9, wherein sodium and magnesium and calcium are present in an amount of less than about 100 ppm.

13. The titanium alloy powder of claim 9, wherein said powder meets ASTM B265 grade 5 chemical specifications.

14. The titanium alloy powder of claim 9, wherein the tap density is in the range of from about 4% to about 11%.

15. The titanium alloy powder of claim 9 agglomerated as seen in Figs. 10-12.

16. The titanium alloy powder of claim 9 formed into a sintered product.

17. A solid object made from the titanium alloy powder of claim 9.

18. A titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 200 ppm and having a tap density in the range of from about 4% to about 11%.

19. The titanium alloy powder of claim 18, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

20. The titanium alloy powder of claim 18, wherein sodium and calcium and magnesium are present in an amount of less than about 100 ppm.

21. The titanium alloy powder of claim 18, wherein said powder meets ASTM B265 grade 5 chemical specifications.

22. The titanium alloy powder of claim 18 agglomerated as seen in Figs A to B.

23. The titanium alloy powder of claim 18 formed into a sintered product.

24. A solid object made from the titanium alloy powder of claim 18.

25. A titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or an alkaline earth metal being present in an amount less than about 200 ppm made by the subsurface reduction of chloride vapor with molten alkali metal or molten alkaline earth metal.

26. The titanium alloy powder of claim 25, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

27. The titanium alloy powder of claim 25, wherein sodium and calcium and magnesium are present in an amount of less than about 100 ppm.

28. The titanium alloy powder of claim 25, wherein said powder meets ASTM B265 grade 5 chemical specifications.

29. The titanium alloy powder of claim 25, wherein the chloride vapor is introduced at greater than sonic velocity into flowing liquid sodium.

30. The titanium alloy powder of claim 25, wherein the tap density is in the range of from about 4% to about 11%.

31. The titanium alloy powder of claim 25 agglomerated as seen in Figs. 10-12.

32. The titanium alloy powder of claim 29 formed into a sintered product.

33. A solid object made from the titanium alloy powder of claim 29.

34. Agglomerated titanium base alloy powder having about 6% by weight aluminum and about 4% by weight vanadium with an alkali or alkaline earth metal being present in an amount less than about 100 ppm substantially as seen in Figs. 10-12.

35. The titanium alloy powder of claim 34, wherein the surface area as determined by BET analysis is at least about 3 square meters per gram after distillation of the powder at temperatures between about 500°C and about 575°C for about 8 to about 12 hours.

36. The titanium alloy powder of claim 34, wherein said powder meets ASTM B265 grade 5 chemical specifications.

37. The titanium alloy powder of claim 34, wherein the tap density is in the range of from about 4% to about 11.

38. The titanium alloy powder of claim 34 formed into a sintered product.

39. A solid object made from the titanium alloy powder of claim 34.

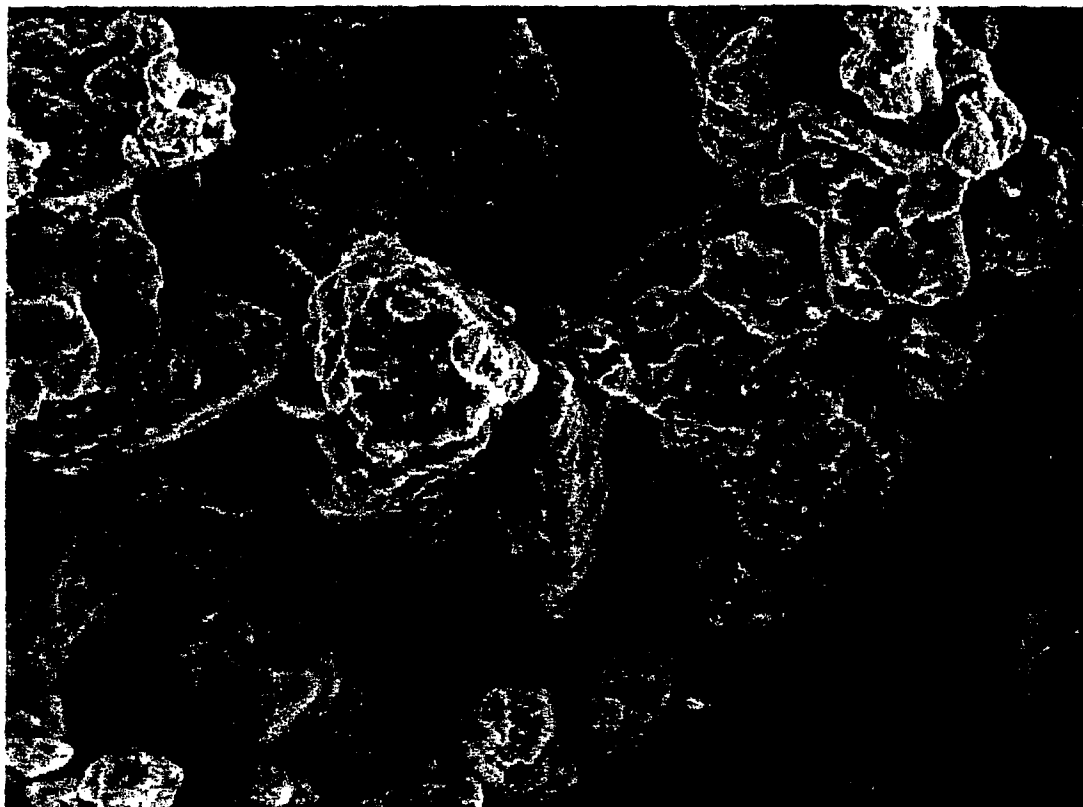


FIGURE 1

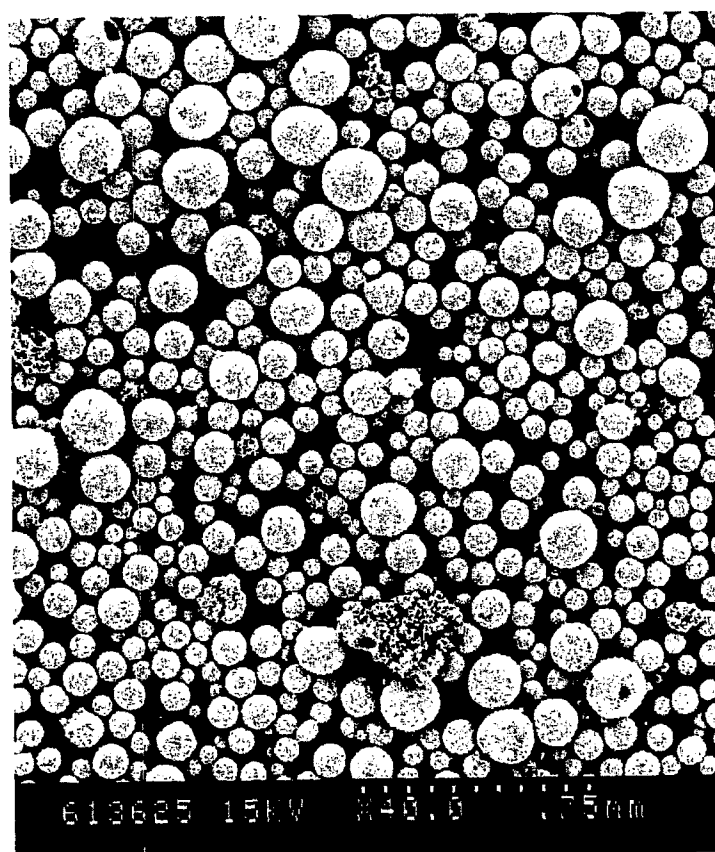
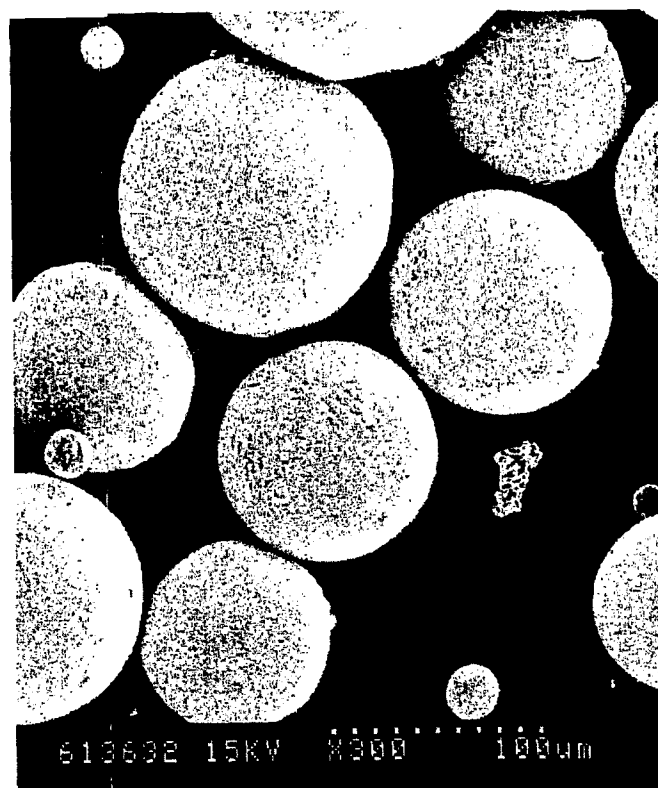


FIGURE 2



FIGURE 3

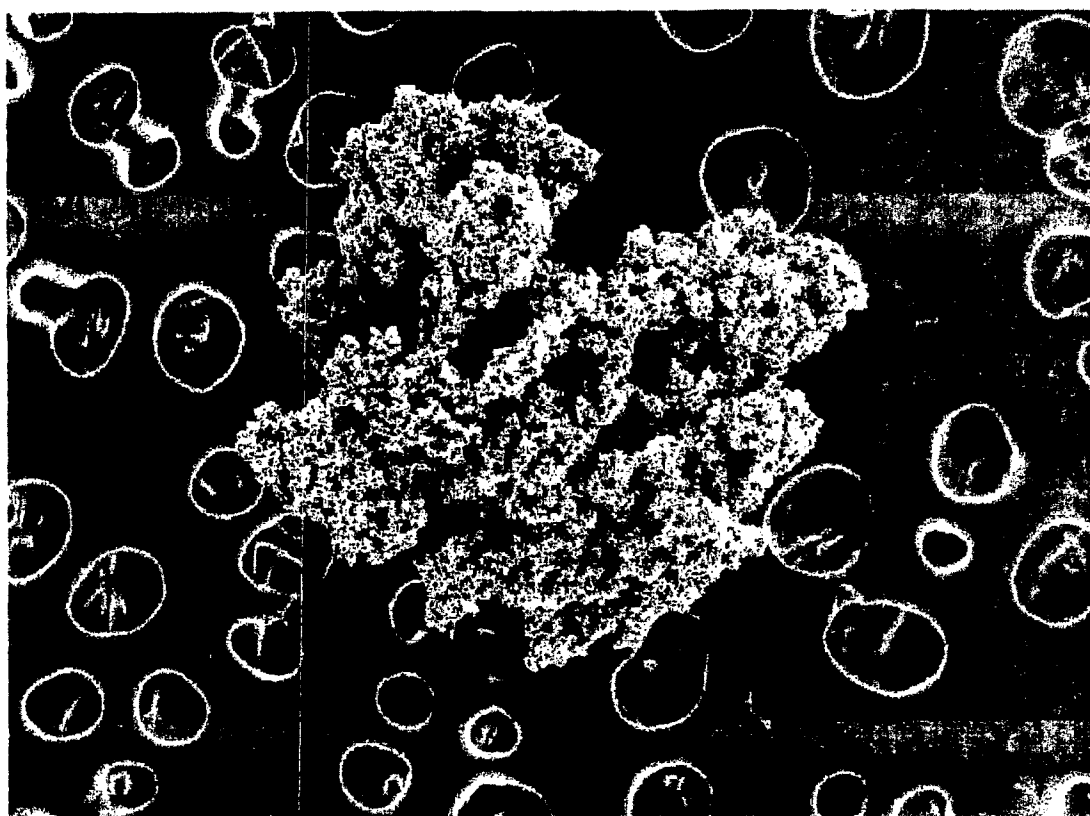


FIGURE 4

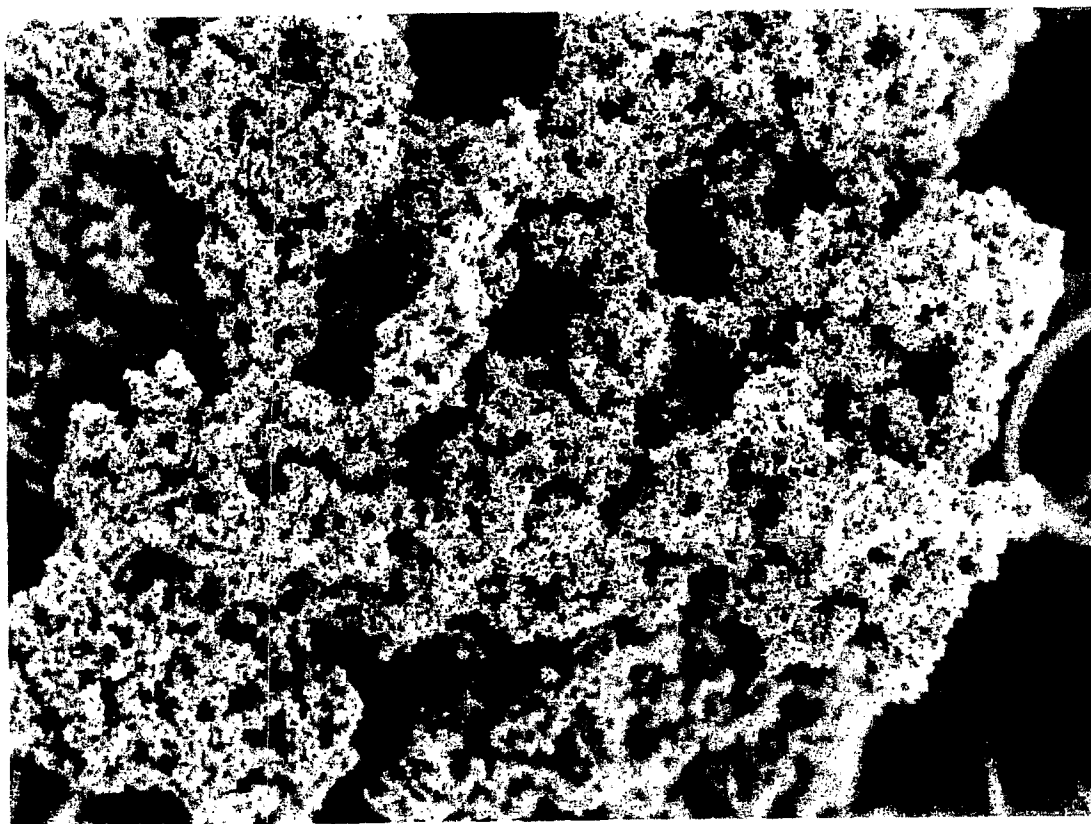


FIGURE 5

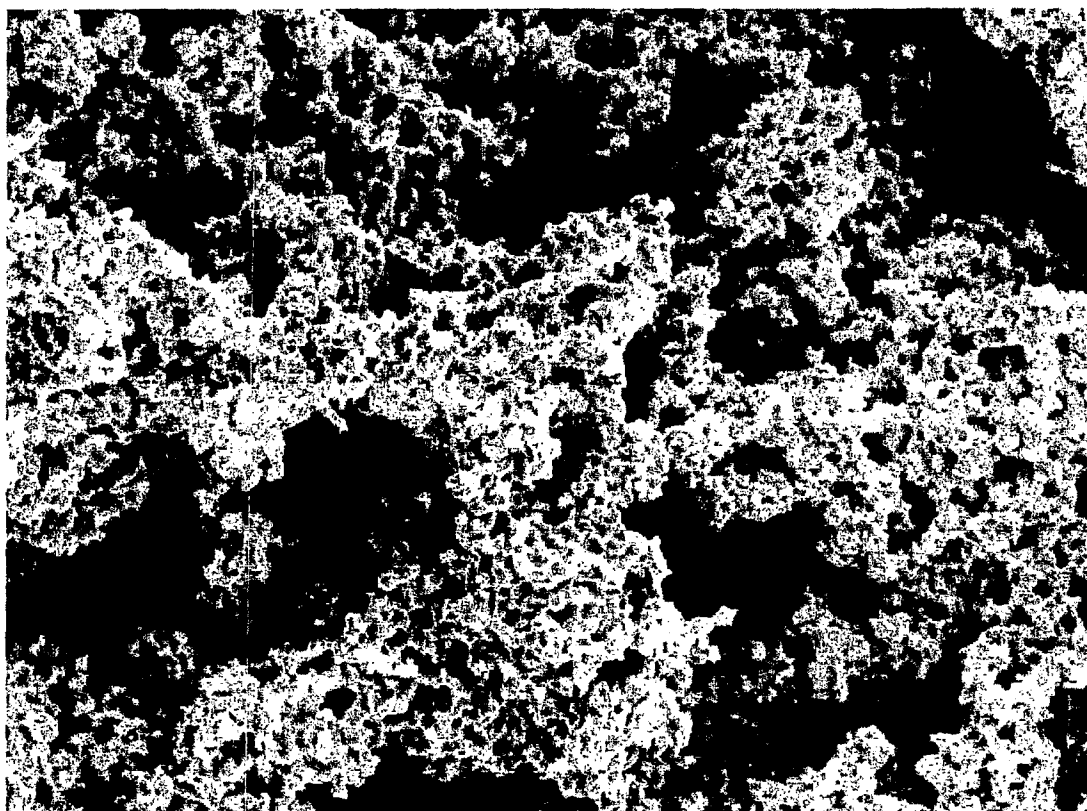


FIGURE 6

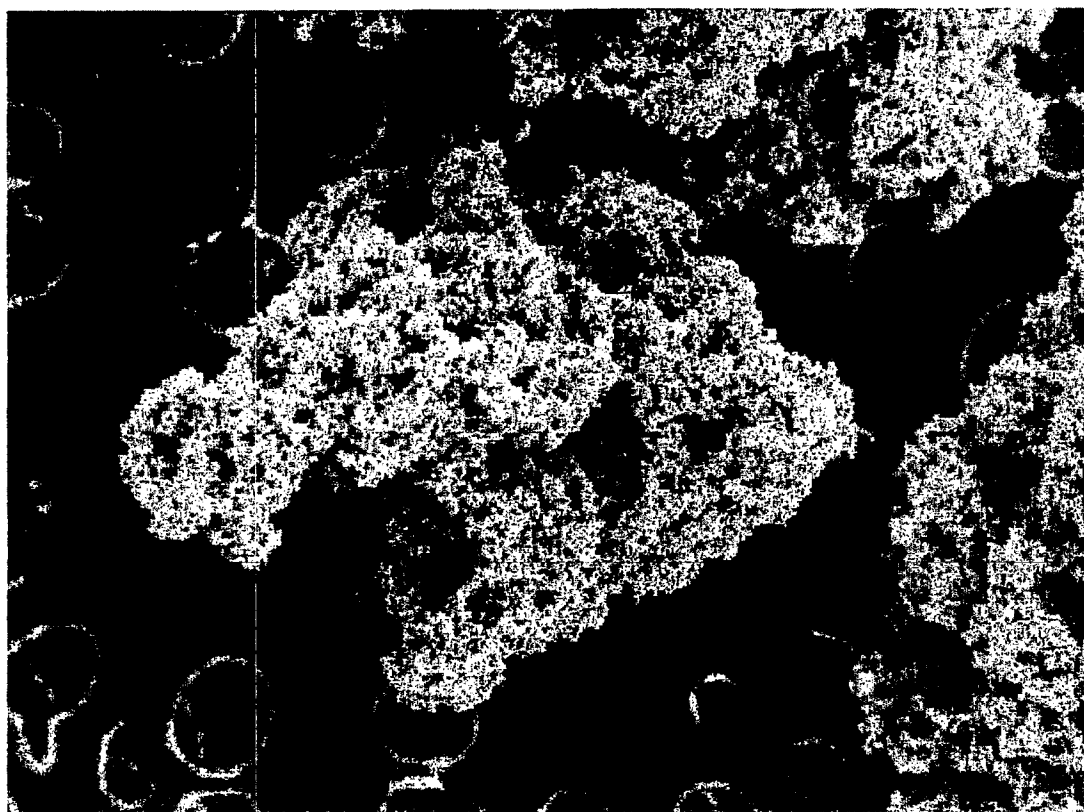


FIGURE 7

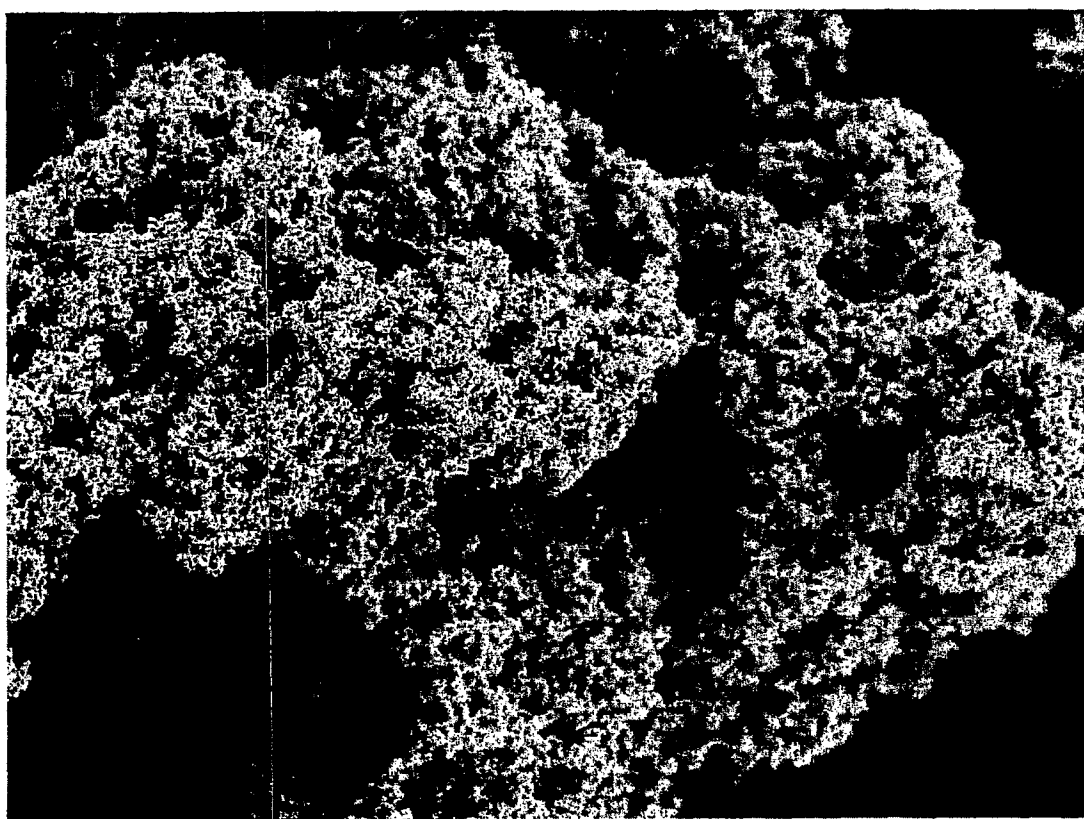


FIGURE 8

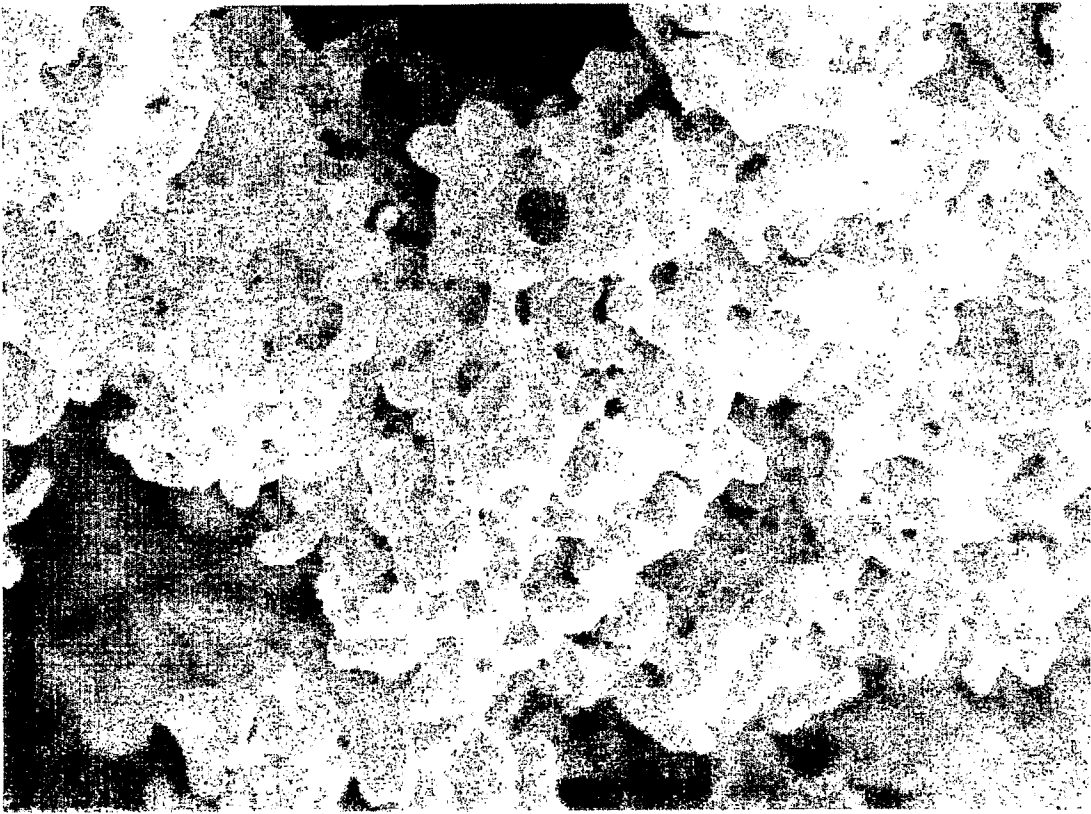


FIGURE 9

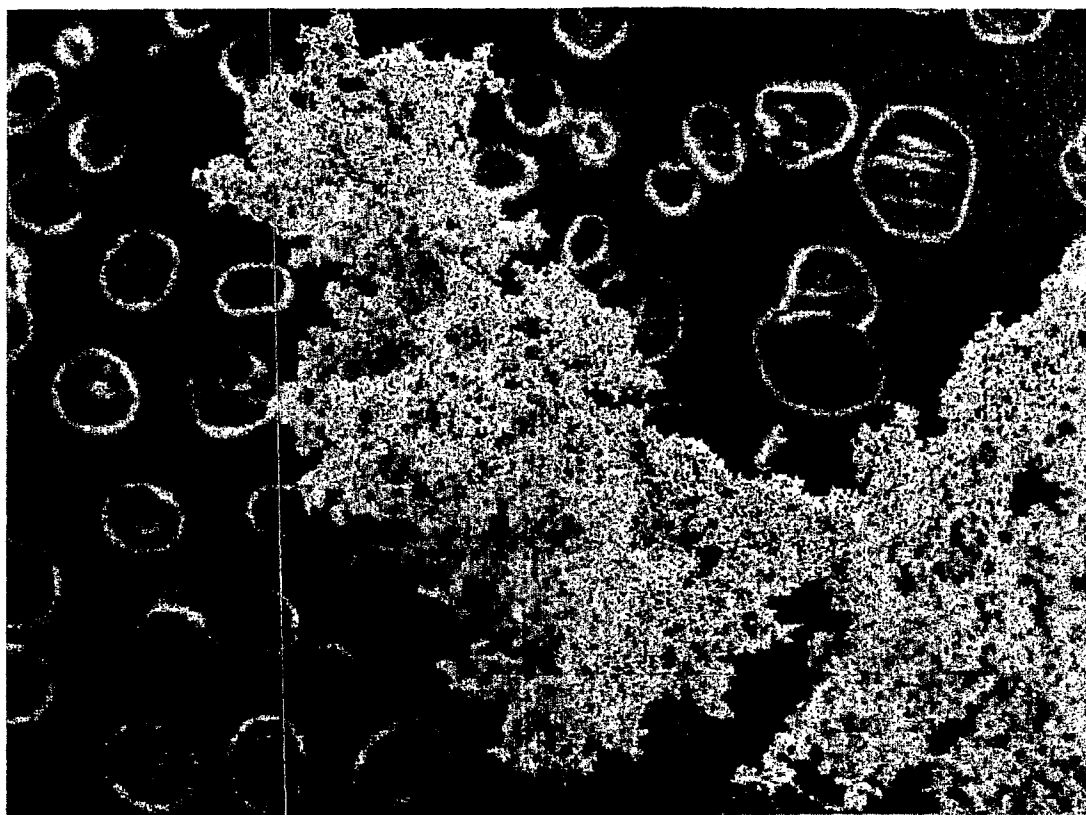


FIGURE 10

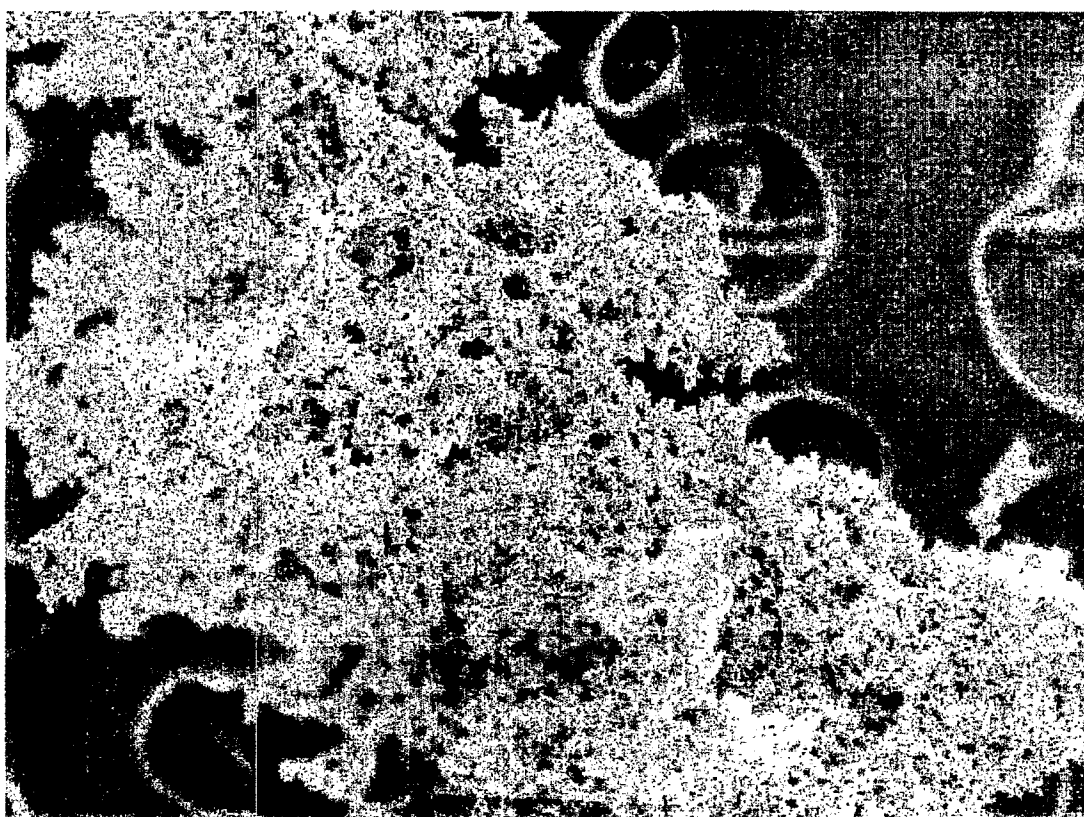


FIGURE 11

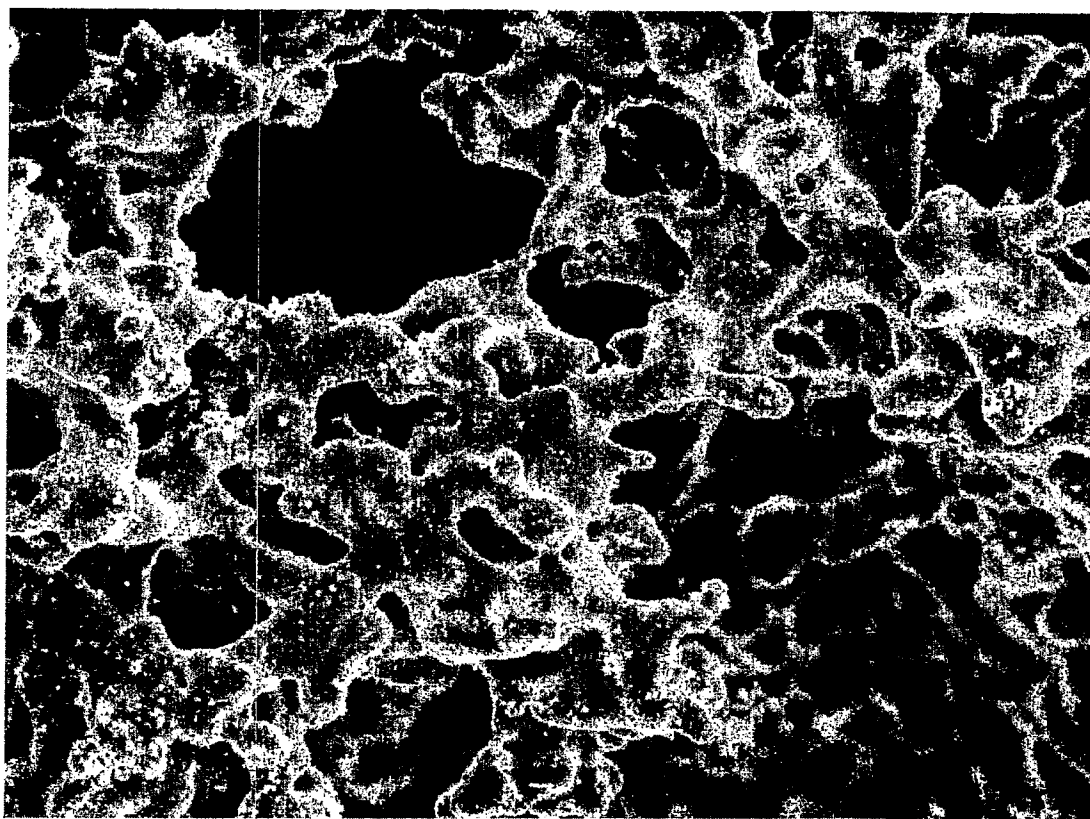


FIGURE 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/028396

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B34/12 C22C1/04 C22C14/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/021807 A2 (INTERNAT TITANIUM POWDER LLC [US]; ARMSTRONG DONN REYNOLDS [US]; ANDER) 10 March 2005 (2005-03-10) page 13, last paragraph; claims 10-13	1-39
X	WO 2005/019485 A (INTERNAT TITANIUM POWDER LLC [US]; ERNST WILLIAM A [US]) 3 March 2005 (2005-03-03) page 20, lines 6-10	1-39
X	US 2002/005090 A1 (ARMSTRONG DONN REYNOLDS [US] ET AL) 17 January 2002 (2002-01-17) paragraph [0019]	1-39
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

21 December 2006

Date of mailing of the international search report

02/01/2007

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Badcock, Gordon

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/028396

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>MAHAJAN, Y. ET AL: "Microstructure Property Correlation in Cold Pressed and Sintered Elemental Ti-6Al-4V Powder Compacts." PUBLISHED BY: TMS/AIME. P.O. BOX 430, 420 COMMONWEALTH DR., WARRENDALE, PA. 15086 CONFERENCE: POWDER METALLURGY OF TITANIUM ALLOYS, LAS VEGAS, NEV., 26-28 FEB. 1980, 1980, XP001248542 experimental</p>	<p>7,8,16, 17,23, 24,33, 34,38,39</p>
A	<p>GERDEMANN, S.J. (ALBANY RESEARCH CENTER (US DOE)) ET AL: "Characterization of a titanium powder produced through a novel continuous process." ADVANCES IN POWDER METALLURGY & PARTICULATE MATERIALS - 2000, PP. 12.41-12.52, GRAPHS, PHOTOMICROGRAPHS, 14 REF. PUBLISHED BY: METAL POWDER INDUSTRIES FEDERATION. 105 COLLEGE RD. EAST, PRINCETON, NJ 08540-6692, USA CONFERENCE: PM2TEC 2000: 2000 INT, 2000, XP001248539 introduction</p>	<p>1-39</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2006/028396

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005021807 A2	10-03-2005	AU 2004269422 A1 CA 2537659 A1	10-03-2005 10-03-2005
WO 2005019485 A	03-03-2005	NONE	
US 2002005090 A1	17-01-2002	NONE	

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 July 2008 (03.07.2008)

PCT

(10) International Publication Number
WO 2008/079115 A1

(51) International Patent Classification:
B22F 9/28 (2006.01) **C22B 34/12** (2006.01)

(74) Agent: **LEVY, Harry, M.**; Emrich & Dithmar, L.L.C., 125 South Wacker Drive, Suite 2080, Chicago, IL 60606 (US).

(21) International Application Number:
PCT/US2006/048828

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:
22 December 2006 (22.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (*for all designated States except US*): **INTERNATIONAL TITANIUM POWDER, L.L.C.** [US/US]; 940 S. Frontage Road, Suite 1400, Woodridge, Illinois 60517 (US).

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

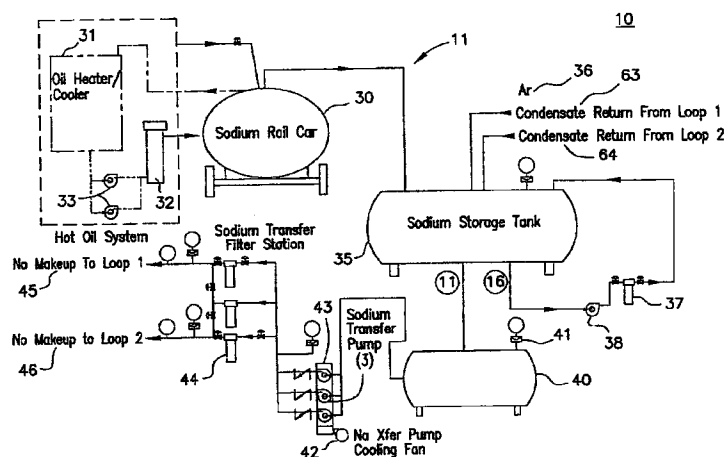
(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **ERNST, William** [US/US]; 7680 Steeple Chase Drive, Frankfort, IL 60423 (US). **JACOBSEN, Lance** [US/US]; 123 San Carlos Road, Minooka, IL 60447 (US).

Published:

— with international search report

(54) Title: DIRECT PASSIVATION OF METAL POWDER



(57) Abstract: A method of producing passivated Ti or Ti alloy particles with oxygen concentrations of less than about 900 parts per million (ppm), which includes introducing a halide vapor of Ti or the metal constituents of the alloy at sonic velocity or greater into a stream of liquid alkali or liquid alkaline earth metal or mixtures thereof forming a reaction zone in which the halide is reduced by the liquid metal present in sufficient excess of stoichiometric such that Ti or Ti alloy powder from the reduction of the halide by the liquid metal is friable. After filtration and distillation excess liquid metal is removed from the Ti or Ti alloy powder that is then maintained at elevated temperature for a time sufficient to grow the particles to average diameters calculated from BET surface area measurement greater than about one micron. After cooling the Ti or Ti alloy powder to temperature of about 800C or less, the cooled Ti or Ti alloy powder is contacted with air and/or water to passivate the particles to produce friable metal powder and to remove other reaction products. A system for accomplishing the method is also shown.

DIRECT PASSIVATION OF METAL POWDER

FIELD OF THE INVENTION

This invention relates to the production of metals and alloys using the Armstrong Process.

BACKGROUND OF THE INVENTION

The present invention relates to the production of metals and alloys using the general method disclosed in U.S. patent nos. 6,409,797; 5,958,106; and 5,779,761, all of which are incorporated herein, and preferably a method wherein titanium or an alloy thereof is made by the reduction of halides in a stream of reducing metal. Although the method disclosed herein is applicable to any of the hereinafter disclosed elements or alloys thereof, the invention will be described with respect to titanium and its alloys, simply because the available supply of titanium in the United States is now insufficient to meet the demand. Moreover, as the cost of titanium and its alloys is reduced by the use of the foregoing method, the demand will increase even beyond that already estimated by the aerospace companies and the Department of Defense.

Titanium is a very plentiful element distributed throughout the world, but it is very costly because of the antiquated methods by which it is produced. As is well known in the art, the Kroll and Hunter processes are the principal processes by which titanium is produced worldwide. Both of these processes are batch processes which produce in the first instance, a fused material of titanium and salt and excess reducing metal, magnesium for the Kroll process and sodium for the Hunter process. This fused material (known as sponge) then must be removed from the containers in which it was made, crushed and thereafter electrolytically purified in repeated steps.

The invention hereinafter described is a refinement of the Armstrong Process disclosed in the above incorporated U.S. patents.

Because titanium is an extremely reactive metal and is produced by the Armstrong Process as a very fine powder, generally with average diameters in the 0.1 to 1 micron range as calculated from BET surface area measurements, it is thereafter maintained at elevated temperature in order to increase the average particle diameter to greater than 1 micron. But, even at the large diameters, the powder is difficult to handle unless it has been passivated. By passivation, it is

meant that a small amount of oxygen is introduced to the powder to form titanium dioxide on the surface so that the powder is not incendiary when exposed to air. Too much oxygen will increase the oxygen content beyond the ASTM specification for CP titanium grade 2 or for ASTM grade 5 titanium, that is 6/4 alloy (6% Al, 4% V by weight with the balance Ti). Heretofore, it was believed that the only practical way to passivate titanium powder was to bleed an inert gas such as argon with a very small percentage of oxygen for a time sufficient to increase the oxygen content on the surface of the powder to prevent spontaneous combustion when exposed to air. The times for passivation were measured in hours and was a design issue for large scale commercial plants based on a continuous process.

However, it has been unexpectedly and surprisingly found that passivation of titanium powder and/or titanium alloy powder can be accomplished by direct exposure to air and/or water and/or brine under certain conditions, which not only decrease the passivation time but also simplifies equipment design, thereby making the process simpler, more efficient and less expensive.

SUMMARY OF THE INVENTION

Accordingly, it is a principal object of the present invention to provide a method of producing passivated friable metal powder without the previous requirements for long periods of passivation.

Another object of the present invention is to provide a method of producing passivated metal powder, comprising introducing a metal halide vapor into a stream of liquid alkali or liquid alkaline earth metal or mixtures thereof forming a reaction zone in which the halide vapor is reduced by the liquid metal present in sufficient excess of stoichiometric such that the metal powder from the reduction of the halide vapor by the liquid metal is friable, separating at least most of the excess liquid metal from the reaction products, growing the metal powder until the particles forming the metal powder have average diameters calculated from BET surface area measurement greater than about one micron, cooling the metal powder, and contacting the cooled metal powder directly with air and/or water and/or brine to passivate and produce friable metal powder.

Another object of the invention to provide a method of producing passivated metal powder, comprising introducing a halide vapor of the metal into a stream of

liquid sodium or liquid magnesium metal forming a reaction zone in which the halide is reduced by the liquid sodium or magnesium metal present in sufficient excess of stoichiometric such that the metal powder formed by the reduction of the halide vapor by the liquid sodium or magnesium metal is friable, separating reaction products from at least most of the excess sodium or magnesium metal, maintaining the metal powder at elevated temperature for a time sufficient to grow the powder until the particles forming the powder have average diameters calculated from BET surface area measurement greater than about one micron, cooling the metal powder to less than about 100°C, and contacting the cooled metal powder with air and/or water and/or brine to passivate and produce friable metal powder.

Yet another object of the invention is to provide a method of producing passivated Ti or Ti alloy powder with oxygen concentrations of less than about 1800 parts per million (ppm), comprising introducing a halide vapor of Ti or the metal constituents of the alloy into a stream of a liquid alkali or a liquid alkaline earth metal or mixtures thereof forming a reaction zone in which the halide is reduced by the liquid metal present in sufficient excess of stoichiometric such that Ti or Ti alloy powder from the reduction of the halide by the liquid metal is friable, separating Ti or Ti alloy powder reaction products from at least most of the excess liquid metal, maintaining the Ti or Ti alloy powder at elevated temperature for a time sufficient to grow the particles forming the Ti or Ti alloy powder to average diameters calculated from BET surface area measurement greater than about one micron, cooling the Ti or Ti alloy powder, and directly contacting the cooled Ti or Ti alloy powder with one or more of air and water and brine to passivate and produce friable powder while maintaining the oxygen concentration below about 1800 ppm.

Still a further object of the invention is to provide a method of producing passivated Ti or Ti alloy particles with oxygen concentrations of less than about 900 parts per million (ppm), comprising introducing a halide vapor of Ti or the metal constituents of the alloy at sonic velocity or greater into a stream of liquid alkali or liquid alkaline earth metal or mixtures thereof forming a reaction zone in which the halide is reduced by the liquid metal present in sufficient excess of stoichiometric such that Ti or Ti alloy powder from the reduction of the halide by the liquid metal is friable, separating by filtration and distillation excess liquid metal from the Ti or Ti

alloy powder at least in part under vacuum, maintaining the Ti or Ti alloy powder at elevated temperature in a vacuum or an inert atmosphere or a combination thereof for a time sufficient to grow the particles forming the powder to average diameters calculated from BET surface area measurement greater than about one micron, cooling the Ti or Ti alloy powder to temperature of about 70°C or less, and contacting the cooled Ti or Ti alloy powder with air to passivate the particles while maintaining the oxygen concentration of the powder below about 900 ppm, and washing the passivated powder to produce friable metal powder and to remove other reaction products.

A final object of the invention is to provide a system producing passivated and friable metal particles, comprising a storage container holding a supply of halide of the metal or alloys to be produced, a storage container holding a supply of reducing metal, pump mechanism establishing a flowing stream of liquid reducing metal, mechanism including nozzles for introducing halide vapor into the flowing stream of liquid reducing metal forming a reaction zone and producing reaction products of metal powder and a halide salt, wherein the liquid metal is present in a stoichiometric excess sufficient to maintain the temperature of the reaction products away from the reaction zone below the sintering temperature of the metal powder, separation equipment including one or more of filtration mechanism, distillation mechanism, mechanism for contacting reaction products with hot and/or cold gas for heating and/or cooling reaction products and for separating reducing metal from the metal powder while growing the particles forming the metal powder to have average diameters calculated from BET surface area measurement greater than about one micron, and mechanism contacting cooled metal powder with air and/or water and/or brine to passivate and produce friable metal powder and to separate the salt from the friable metal powder.

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of facilitating an understanding of the invention, there is illustrated in the accompanying drawings a preferred embodiment thereof, from an inspection of which, when considered in connection with the following description, the invention, its construction and operation, and many of its advantages should be readily understood and appreciated.

FIGURES 1-4 are schematic representations of various portions of the system and equipment used in the method herein described to produce friable passivated metal powder.

DETAILED DESCRIPTION OF THE INVENTION

Referring to the drawings, there is disclosed a system 10 from which is produced friable and passivated metal powder. The metals and the alloys of which may be made according to the system hereinafter described are Ti, Al, Sn, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, Si or alloys thereof, all as previously disclosed in the above referenced and incorporated patents. The system 10 includes a sodium supply system 11, a chloride supply system 12, a reactor 15, a distillation system 16, a growing system 17, a cooling system 18, a washing system 19 and a drying system 21.

Although described herein with respect to chlorides and sodium reducing metal, it is clear that any halide may be used and a wide variety of alkali and alkaline earth metals or mixtures may be used. Commercially, sodium and magnesium are the most common reducing metals in the reduction of, for instance, titanium. Calcium has been used as a reducing metal in Russia. Although the system hereinafter described is specific to the chloride and to sodium, it is specifically intended that the invention is not so limited.

The sodium system 11 includes a sodium source 30 such as a common rail car, which is in communication with a heater 31 in order to liquify the sodium. The sodium heating system includes filters 32 with the requisite pumps 33 necessary to liquify sodium in a rail car 30 for transfer to sodium storage or an intermediate tank 35. The storage or intermediate tank 35 is provided with an inert atmosphere such as argon and is connected to a sodium substorage tank 40 which is provided with a pressure transmitter 41. Because the sodium in sodium storage tank 35 is liquid,

there is a recirculation loop provided through filter 37 and a pump 38 which simply circulate sodium while it remains in the sodium storage tank and of course, there is provided the usual temperature sensors, pressure sensors and other engineering devices, not shown for purposes of clarity and brevity.

As used in the drawings, PT is a pressure transmitter, PSV is a relief valve; PSE is a rupture disc; PSH is a pressure switch; FT is a flow transmitter and CV is a flow control valve. These standard engineering sensors and controls will not be further described.

The sodium supply system 11 further includes a cooling fan 42 in conjunction with a series of sodium transfer pumps 43 which may be electromagnetic and filters 44 for pumping sodium from the storage tanks 35 and 40 to a sodium make-up 45 for loop one, and sodium make-up 46 for loop 2.

The system 10 is configured for two reactor modules as each reactor module can produce 2 million pounds of titanium or titanium alloy, or other metal alloys as previously set out, per year, so that a 4 million pound a year plant would have two operational reactors 15, whereas a 40 million pound plant would have 20 operational reactors 15.

As seen particularly in Figs. 1 and 3, sodium from the make-up loop 45, 46 is introduced via pumps 47 and cooling fan 48 into a series of filters 49 and heat exchanger 50 into the reactor 15. A head tank 52 for sodium is also included in the system 10 and is in communication with the line in both the make-up loops 45, 46. Finally, the sodium supply system 11 includes condenser drains 53 and 54 which are in communication with the reaction products that come out of the reactor 15, as seen in Fig. 3 along with a condenser 55 that is connected by a sodium condenser vapor header 56, a cooling fan 57 and a condensate reservoir 58. A condenser vacuum pump 61 and a condensate return pump 62, connected to the condensate return 63 and/or condensate return 64 are in communication with the storage tank 35, all as will be hereinafter explained, to complete the Na loop.

Referring to Fig. 2, there is disclosed the halide or chloride supply system 12 in further detail and includes for titanium tetrachloride feedstock, a titanium tetrachloride day tank 70 in communication with a much larger supply of titanium tetrachloride, not shown. The tank 70 is in communication via a series of pumps 71

with a pair of titanium tetrachloride boilers 73 and 74, each of which has its own heater 76. As previously stated, the description herein is for a two reactor 15 system, that is two modules as shown in the incorporated patents, therefore, there is as described, two boilers, one for each reactor. It is clear to one of ordinary skill in this art that should there be more reactors, there will be more boilers and if an alloy is to be produced, there will be boilers for each alloy constituent.

For an alloy such as the most commonly used 6/4 titanium alloy consisting essentially of 6% aluminum and 4% percent vanadium and described as ASTM B 265, grade 5, Ti 5 alloy, there has to be provided a vanadium chloride boiler 83 and a vanadium chloride boiler 84 connected by pumps 81 to a vanadium chloride day tank 80. Each of the vanadium chloride boilers 83 and 84 is provided with its own heater 86 and is connected by various piping manifolds to the reactors 15 as hereinafter will be set forth. Similarly, a aluminum chloride day tank 90 is provided and is connected by a series of valves 91 to aluminum chloride boilers 93 and 94. Each of the boilers 93 and 94 is provided with a heater 96 and unloading tank 97 and scales 98 in order to weigh the amount of aluminum chloride which is used in the production of the alloy. The difference between the system for aluminum chloride and vanadium chloride is that aluminum chloride is a solid at room temperature and may be transmitted as a solid through the valves 91 from the day tank 90 to the boilers 93. The scales 98 are used to ensure the correct amount of aluminum chloride is thereafter provided to the boilers 93 and 94. As indicated, the various halides or chlorides of the alloy constituents are fed from the boilers via pipes, valves and the like to a common pipe or manifold prior to the entry into the associated reactor 15 with the liquid reducing metal such as, but not limited to liquid sodium or liquid magnesium flowing there through.

Referring now to Figure 3, the liquid reducing metal such as sodium from the heater exchanger 50 is introduced into the reactor 15 as a stream and the metal chloride(s) is introduced into the stream of liquid reducing metal at at least sonic velocity in order to prevent back-up of the liquid metal into the halide supply and there is produced in the reactor a reaction product of metal powder which may be an alloy, a salt and the excess reducing metal present. As understood, the ratio of excess to stoichiometric reducing metal to the amount of halide will enable the

steady state reaction temperature to be maintained at prescribed values, a short distance downstream from the reaction zone which is produced when the vapor halide is injected or introduced into the stream of molten metal. The exact temperatures inside the reaction zone are unknown, but a few inches downstream, the steady state temperatures have been measured and controlled anywhere from about 800° C to about 300° C or less for sodium and titanium tetrachloride. The stoichiometric excess preferably is between 10 and 100 times that necessary to produce the metal powder, the greater excess of metal the lower the steady state temperature will be. There is an engineering trade-off between running at higher temperatures and using additional excess liquid reducing metal to maintain a lower steady state temperature, all of which is within the ordinary skill of the art. Should magnesium be used rather than sodium, then higher running temperatures will be required because of the melting temperature of magnesium.

The reactor 15 is operated in a protective atmosphere and preferably in an argon atmosphere. Alternative inert gases such as helium may be used. The reaction products from the reactor are connected to a filter 110 which permits liquid reducing metal to be drawn therefrom into the head tank 52 and then back into the sodium supply system 11.

The filter 110 is provided with a valve 111 and is connected to a vacuum system 112 so that a collection pipe 115 surrounded on one side by valve 111 and on the other side by valve 114 is under vacuum and sodium draining from the reaction products slurry of metal powder and salt is directed through a filter (not shown) to a line to condenser drain 53 and hence back to the sodium supply system 11.

From the collection pipe 115 the material, now free of most of the sodium or liquid reducing metal, is introduced into a distillation screw conveyor 120, the screw conveyor being provided with an outlet 125 or collection pipe and two valves 121 and 123, so as to connect the distillation screw conveyor to a vacuum system 122 and insulate the distillation conveyor from the heat treatment calciner 130, as will be explained.

As material is moved by the distillation conveyor 120 in the form of an auger, sodium drained from the distillation conveyor 120 is conducted via a line to

condenser drain 54 and returned to the sodium supply 11. Since the distillation screw conveyor 120 is connected by a header 56 to the condenser 55, cooling fan 54 and condensate reservoir 58, the reducing metal vapor is removed in the distillation screw conveyor and again returned as previously described by the pumps 62 to the sodium supply system 11.

It is clear that the majority of the excess sodium in this system is removed from the product and returned to the sodium supply system leaving only entrained sodium and sodium used in the production of the salt which is lost. The salt may or may not be split electrolytically to recirculate the sodium, depending on economics.

The growing station 17 is illustrated particularly in Fig. 3 and includes a rotating drum calciner 130 connected to the outlet of the distillation conveyor 120 via the valves 121 and 123. The calciner 130 rotates, as is known in the art, and material therein after a residence time predetermined by engineering principles is transmitted via an outlet 131 to the cooling and passivation system 18 which includes a screw conveyor having an outlet 136. The cooling conveyor 135 uses oil cooling as does a majority of other heat exchangers in the subject system 10 due to the presence of liquid sodium or liquid magnesium, both of which would be explosively reactive in the presence of water. Because the material in the calciner 130 is at elevated temperature, it should be present either a protective atmosphere such as an inert gas, preferably argon.

The cooling and passivation conveyor 135 reduces the temperature of the material therein from the temperature in the calciner 130 which preferably is somewhat in the excess of 700°C preferably about 750°C, down to less than 100°C at the outlet 136 and preferably about 80°C or less. At this point in the process, almost all of the sodium except for that entrained within the particles has been removed, and the remaining reaction products, that is a mixture of salt and metal powder, are conveyed to the cake silo diverter valve 139 and hence through outlets 141 and 142 to the cake storage silo 151 and 152, as best seen in Fig. 4. The cake is accumulated in the storage silos until the rotary valves 153 and 154 are operated to send the material via a diverter 156 or 157 to a cake slurry tank 160, wherein the cake is formed into a slurry by means of a water supply 161 connected to the tank forming a slurry therein which is then introduced into a vacuum belt filter 170 that is

connected to a vacuum system 178. Water for the slurry formed in the slurry tank 160 is provided from a supply 161 which is passed through a filter 162 and a variety of optional deionization columns 163 into a clean water tank 165. Clean water from the tank 165 flows to the cake slurry tank 160 and to the outlet portion of the vacuum belt filter 170. The vacuum belt filter 170 is contained within a housing 171 and has spray nozzles longitudinally spaced there along connected to an intermediate brine wash tank 167 and a concentrated brine wash tank 168 by suitable pumps 173. Water or brine draining through the powder on the conveyor 170 is either returned via a pump 174 to the appropriate tank 168 or to a brine discharge facility or system, not shown. As seen, powder on the conveyor belt filter 170 is initially contacted with brine and thereafter with water having lesser concentrations of salt until finally contacted with clean water from tank 165, which may be heated.

The cake silos 151, 152 are at temperatures less than 100 °C preferably 80°C or less, and most preferably 40° - 80°C. The washed powder outlet chute 177 connected to the vacuum belt filter 170 directs powder which has been passivated and washed with water and/or brine to an inerted turbo dryer 180. A fines collection filter press 179 is in communication with the powder conveyor housing 171 near the outlet chute 177 to collect fines from the conveyor 170.

The inerted turbo dryer 180 is connected to a condenser 181, a condenser fan 182 and condensate return pump 183 through which the moisture is removed from the passivated and now friable powder, the moisture being returned or disposed of as economics dictate. The inerted turbo dryer 180, as previously stated, is under a protective atmosphere such as argon or nitrogen, and therefore, an argon or nitrogen inlet 185 is connected to protection to the powder after passivation while it is at elevated temperatures.

Finally, a product outlet 190 leads from the turbo dryer 180 to a series of drums 192 which may be stationed beneath the outlet 190 and filled at a rate according to the system design.

Operationally, and by way of example only, without limiting the invention, the sodium storage tank is preferably maintained at an elevated temperature so that the sodium therein is liquid. The melting point of sodium is about 98°C. so that the sodium storage tanks 35 and 40 are maintained about 105°C whereas the sodium

head tank 52 is maintained at about 125 - 300°C, preferably about 125°C. Exact temperatures and/or pressures hereinafter set forth are subject to engineering considerations so the ranges are by way of example only and are not intended to limit the invention.

The titanium tetrachloride boilers 73, 74 are maintained at about 220°C resulting in pressures of about 500 kPa but may be at pressures up to about 800 kPa. Both the vanadium chloride boilers 83, 84 as well as aluminum chloride boilers 93, 94 are maintained at pressures greater than the titanium tetrachloride boilers because the vapors from each of the alloy constituent boilers have to be at pressures greater than the titanium chloride boilers so as to prevent titanium chloride from backing up into the alloy constituent boilers. For instance, if the titanium tetrachloride boilers 73, 74 are at 500 kPa, then the VCl_4 , AlCl_3 boilers are maintained at about 800 kPa.

The reactor 15 may be operated with an inlet temperature of about 260°C with the outlet temperature about 100° C greater, or about 360°C. Higher or lower inlet temperatures are possible. The distillation conveyor 120 is preferably, but not necessarily, operated at about 538° C but may be operated from about 450°C up to about 550°C depending on the vacuum value of the system, the better the vacuum the lower the distillation temperature can be. The calciner 130 is preferably operated at about 750°C for approximately 6 hours in order to grow the metal particles forming the powder. Again, engineering considerations are taken into account between the equipment size, residence time and the temperature at which the particle growth is maintained. Temperatures of 700° or above are practical, but again, the lower the temperature, the longer the residence time in order to achieve the same particle growth. The cooling passivation conveyor 135 preferably has an inlet temperature which is generally equal to the outlet temperature of the calciner 130 such as about 750° and an outlet temperature preferably in the range of between about 40° C to 80° C. The higher the outlet temperature the greater the oxygen pick-up of the metal powder, but temperatures in the range of from about 40° C to about 80° C are preferred with 40°C providing better results than the 80°C temperature.

The cooling and heating in the system 10 is by means of heat transfer through coils in which oil is used as a heat transfer medium for safety considerations. The

silos 151 and 152 are generally operated at ambient temperatures in air and stay principally at the temperatures in which the powder is introduced from the conveyor 135, that is in the range between about 40 °C and 80 °C. Washing after air passivation or directly without air passivation is done at ambient temperature and the last wash, that is water from the fresh water tank 165 may be warmed to facilitate dissolving salt and warming the powder for entry into the inerted turbo dryer 180.

Generally, the powder entering the turbo dryer 180 is at a temperature in the range of from ambient water tap temperature to about 70 °C.

Finally, the powder leaving the inerted turbo dryer 180 at the outlet 190 is preferably at a temperature of about 60 °C at which the powder is not too reactive, it being understood that at higher temperatures, powder is more reactive than at lower temperatures, particularly powder in the 1-10 micron range, which is the preferred particle size as determined by BET measurement after the particles forming the powder exit the calciner 130. As understood from the incorporated patents, metal particles coming out of the reactor 15 generally have average diameters in the range of from about 0.1 to about 1 micron as calculated from BET surface area measurement. However, these particles are too small for many powder metallurgy usages and therefore, need to be grown which is the purpose of the calciner 130. Although maintaining the powder at elevated temperatures causes the particles to grow so that some growth takes place in the filter 115, the distillation conveyor 120 and thereafter during transfer to the heat calciner 130, the majority of the particle growth occurs in the calciner 130, with temperatures for CP titanium or titanium 6/4 alloy of about 750°C and a residence time of about 6 hours. The system 10, can be designed for various production rates and the equipment dimensions and operating conditions will change as will be understood by an engineer of ordinary skill in this art. Although argon has been indicated as the preferred inert gas, if the temperatures are maintained low enough, nitrogen can be used without deleteriously affecting the powder as well as neon or other inert gases. Although designed herein without blowers, the cake silos 151 and 152 may need blowers in order to circulate additional air to passivate the cake produced from the cooling and passivation conveyor 135. Moreover, passivation could take place by means of contacting the powder after cooling with a mixture of an inert gas and up to about 20% oxygen in

countercurrent relationship, but the method before described is preferred.

It should be understood that material entering the cooling and passivation conveyor 135 is under a protective atmosphere from the heat treatment calciner 130 but exits through the conveyor exit 136 at lower temperatures and with some air being present. An alternative method for passivation is to introduce the powder directly into the washing and drying system 19 rather than using first air passivation and thereafter washing. It is preferred to use air passivation first and then washing after passivation, but it may be preferable for reasons of cost and economy, immediately to wash after the powder comes out of the cooling passivation conveyor 135. Although air passivation followed by washing provides a lower oxygen concentration, for instance 900 ppm for CP titanium, that corresponds to ASTM B265 grade 1 titanium, whereas direct water washing (water and/or brine) without air passivation has provided oxygen concentrations of about 1800 ppm. The lower oxygen content may not always be required, depending upon the end use of the powder. Therefore, either water and/or brine passivation directly or air passivation directly may be employed or a combination thereof, that is air passivation followed by washing in which some passivation be used.

While the invention has been particularly shown and described with reference to a preferred embodiment hereof, it will be understood by those skilled in the art that several changes in form and detail may be made without departing from the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A method of producing passivated metal powder, comprising introducing a metal halide vapor into a stream of liquid alkali or liquid alkaline earth metal or mixtures thereof forming a reaction zone in which the halide vapor is reduced by the liquid metal present in sufficient excess of stoichiometric such that the metal powder from the reduction of the halide vapor by the liquid metal is friable, separating at least most of the excess liquid metal from the reaction products, growing the metal powder until the particles forming the metal powder have average diameters calculated from BET surface area measurement greater than about one micron, cooling the metal powder, and contacting the cooled metal powder directly with air and/or water and/or brine to passivate and produce friable metal powder.
2. The method of claim 1, wherein the metal is one or more of Ti, Al, Sn, Sb, Be, B, Ta, Zr, V, Nb, Mo, Ga, U, Re, Si or alloys thereof.
3. The method of claim 2, wherein the separation includes distillation under vacuum and the powder is held at elevated temperature under vacuum or under an inert atmosphere until the average particle size of the metal powder calculated from BET surface area measurement is at about one micron.
4. The method of claim 2, wherein the separation includes contact with an inert gas sweep and the powder is held at elevated temperature until the average particle size of the metal powder calculated from BET surface area measurement is at least about one micron.
5. The method of claim 2, wherein the metal powder is moving during at least most of the growing and cooling.
6. The method of claim 2, wherein separation includes filtration and the powder is mostly moving after filtration before washing.
7. The method of claim 1, wherein the metal powder is washed by contact with brine and/or water while the metal powder is transported by a filter belt.
8. The method of claim 1, wherein the metal powder is partly washed by contact between the metal powder and differing concentrations of brine.

9. The method of claim 1, wherein the reduction occurs at greater than atmospheric pressure.

10. The method of claim 1, wherein the metal powder is an alloy and the halide is a chloride.

11. The method of claim 7, wherein the washed metal powder is dried under an inert atmosphere.

12. A method of producing passivated metal powder, comprising introducing a halide vapor of the metal into a stream of liquid sodium or liquid magnesium metal forming a reaction zone in which the chloride is reduced by the liquid sodium or magnesium metal present in sufficient excess of stoichiometric such that the metal powder formed by the reduction of the halide vapor by the liquid sodium or magnesium metal is friable,

separating reaction products from at least most of the excess sodium or magnesium metal,

maintaining the metal powder at elevated temperature for a time sufficient to grow the powder until the particles forming the powder have average diameters calculated from BET surface area measurement greater than about one micron, cooling the metal powder to less than about 100°C, and

contacting the cooled metal powder with air and/or water and/or brine to passivate and produce friable metal powder.

13. The method of claim 12, wherein the metal powder is a transition metal or an alloy thereof.

14. The method of claim 13, wherein the transition metal is Ti or an alloy thereof.

15. The method of claim 14, wherein the reaction occurs at a pressure of from about one to about three atmospheres.

16. The method of claim 12, wherein the separation of most of the liquid sodium or magnesium metal from the reaction products includes filtration and/or distillation.

17. The method of claim 12, wherein the metal powder is maintained at a temperature of not less than about 700°C for at least a portion of the growth of the powder particles.

18. The method of claim 17, wherein the powder is cooled on a conveyor from elevated temperature to not greater than about 80°C prior to passivation.

19. The method of claim 18, wherein the metal powder is first passivated with air and thereafter washed with brine and/or water.

20. The method of claim 19, wherein most of the passivation and washing occur while the metal powder is on a conveyor.

21. The method of 20, wherein at least a portion of the growth in size of the powder occurs in a rotatable drum.

22. The method of claim 19, wherein the friable metal powder is dried in an inert atmosphere after washing.

23. A method of producing passivated Ti or Ti alloy powder with oxygen concentrations of less than about 1800 parts per million (ppm), comprising introducing a halide vapor of Ti or the metal constituents of the alloy into a stream of a liquid alkali or a liquid alkaline earth metal or mixtures thereof forming a reaction zone in which the halide is reduced by the liquid metal present in sufficient excess of stoichiometric such that Ti or Ti alloy powder from the reduction of the halide by the liquid metal is friable,

separating Ti or Ti alloy powder reaction products from at least most of the excess liquid metal,

maintaining the Ti or Ti alloy powder at elevated temperature for a time sufficient to grow the particles forming the Ti or Ti alloy powder to average diameters calculated from BET surface area measurement greater than about one micron, cooling the Ti or Ti alloy powder, and

directly contacting the cooled Ti or Ti alloy powder with one or more of air and water and brine to passivate and produce friable powder while maintaining the oxygen concentration below about 1800 ppm.

24. The method of claim 23, wherein the water is de-ionized prior to washing.

25. The method of claim 23, wherein the water is de-oxygenated prior to washing.

26. The method of claim 23, wherein passivation is principally with air and the oxygen concentration in the passivated Ti or Ti alloy is less than about 900 ppm.

27. The method of claim 26, wherein passivation is followed by washing with brine and/or water.

28. The method of claim 23, wherein the Ti or Ti alloy powder is held at an elevated temperature for a time sufficient to grow the particles forming the powder to average diameters calculated from BET surface area measurement in the range of from about 1 to about 10 microns.

29. The method of claim 23, wherein the Ti or Ti alloy powder is held at an elevated temperature of at least about 700°C during at least most of the growing times.

30. The method of claim 23, wherein the powder is cooled to temperature of about 80°C or less before the powder is passivated.

31. The method of claim 23, wherein the reaction products include salt transported with the metal powder until washed.

32. The method of claim 23, wherein the halide vapor includes a chloride, the liquid metal includes sodium or magnesium and the temperature of the liquid metal downstream from the reaction zone is about 200°C above the melting point of the reducing metal.

33. The method of claim 32, wherein the method is mostly continuous.

34. The method of claim 33, wherein the separation is at least in part by distillation conducted under vacuum at temperatures of less than about 550°C when the reducing metal is sodium.

35. The method of claim 33, wherein the separation is at least in part by passing a hot inert gas in contact with at least some of the reaction products to remove some of the entrained reducing metal.

36. The method of claim 33, wherein the liquid metal is sodium.

37. The method of claim 36, wherein the Ti metal or Ti alloy is continuously moving during most of the growing and cooling.

38. The method of claim 37, wherein the liquid sodium is at a temperature of less than about 300°C prior to introduction of the halide vapor and the liquid sodium is maintained at a temperature of less than about 400°C downstream from the reaction zone until separation begins.

39. A method of producing passivated Ti or Ti alloy particles with oxygen concentrations of less than about 900 parts per million (ppm), comprising introducing a halide vapor of Ti or the metal constituents of the alloy at sonic velocity or greater into a stream of liquid alkali or liquid alkaline earth metal or mixtures thereof forming a reaction zone in which the halide is reduced by the liquid metal present in sufficient excess of stoichiometric such that Ti or Ti alloy powder from the reduction of the halide by the liquid metal is friable,

separating by filtration and distillation excess liquid metal from the Ti or Ti alloy powder at least in part under vacuum,

maintaining the Ti or Ti alloy powder at elevated temperature in a vacuum or an inert atmosphere or a combination thereof for a time sufficient to grow the particles forming the powder to average diameters calculated from BET surface area measurement greater than about one micron,

cooling the Ti or Ti alloy powder to temperature of about 80°C or less, and contacting the cooled Ti or Ti alloy powder with air to passivate the particles while maintaining the oxygen concentration of the powder below about 900 ppm, and washing the passivated powder to produce friable metal powder and to remove other reaction products.

40. The method of claim 39, wherein de-ionized and/or de-oxygenated water is used in washing as well as brine in varying concentrations.

41. The method of claim 40, wherein the liquid reducing metal is sodium present in the range of from about 10 to about 100 times the stoichiometric amount.

42. The method of claim 41, wherein the liquid sodium is at a temperature of less than about 300°C prior to introduction of the halide vapor and the liquid sodium is maintained at a temperature of less than about 400°C downstream from the reaction zone until separation begins.

43. The method of claim 42, wherein the powder is heated to an elevated temperature at least about 700°C under an inert atmosphere for a time sufficient such that the average diameters of the particles forming the powder calculate from BET surface area measurement is in the range of from about 1 to about 10 microns.

44. The method of claim 43, wherein the powder is maintained in an inert atmosphere during most of the cooling until passivation begins.

45. Titanium powder produced according to the method of claim 44.

46. Titanium alloy powder including about 6% Al and about 4% V produced according to the method of claim 44.

47. A system producing passivated and friable metal particles, comprising a storage container holding a supply of halide of the metal or alloys to be produced, a storage container holding a supply of reducing metal,

pump mechanism establishing a flowing stream of liquid reducing metal, mechanism including nozzles for introducing halide vapor into the flowing stream of liquid reducing metal forming a reaction zone and producing reaction products of metal powder and a halide salt,

wherein the liquid metal is present in a stoichiometric excess sufficient to maintain the temperature of the reaction products away from the reaction zone below the sintering temperature of the metal powder,

separation equipment including one or more of filtration mechanism, distillation mechanism, mechanism for contacting reaction products with hot and/or cold gas for heating and/or cooling reaction products and for separating reducing metal from the metal powder while growing the particles forming the metal powder to have average diameters calculated from BET surface area measurement greater than about one micron, and

mechanism contacting cooled metal powder with air and/or water and/or brine to passivate and produce friable metal powder and to separate the salt from the friable metal powder.

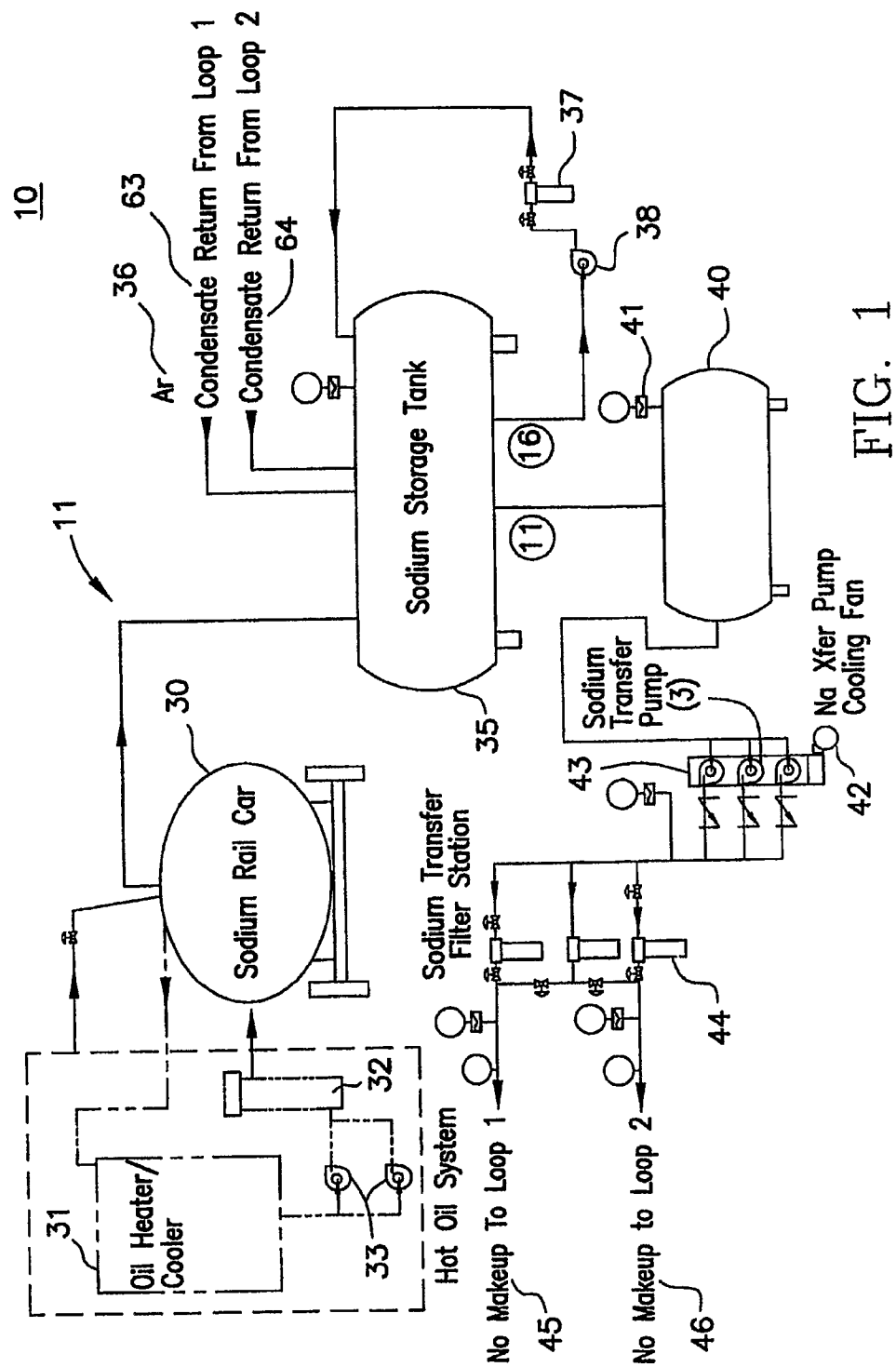


FIG. 1

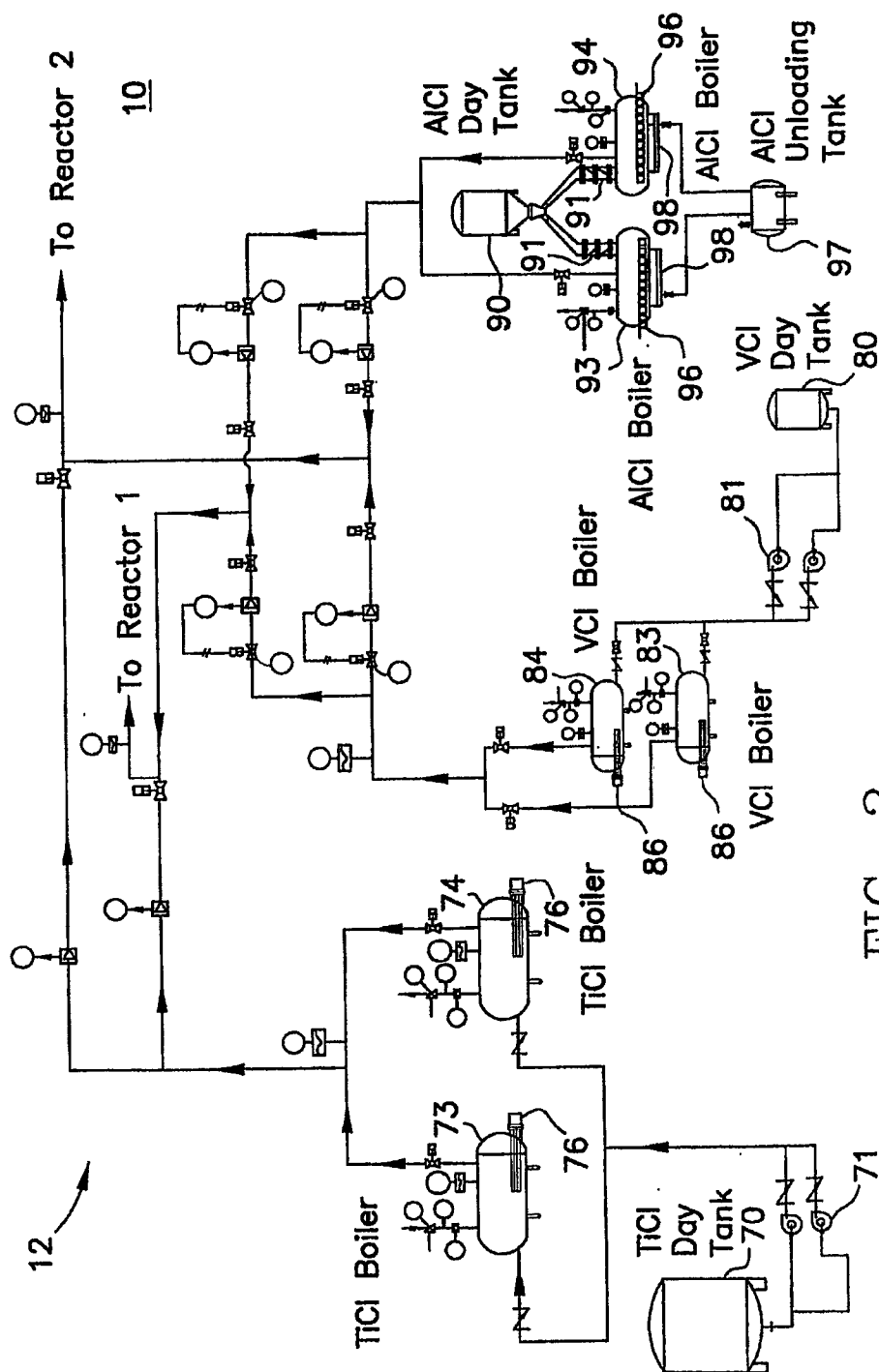


FIG. 2

3/4

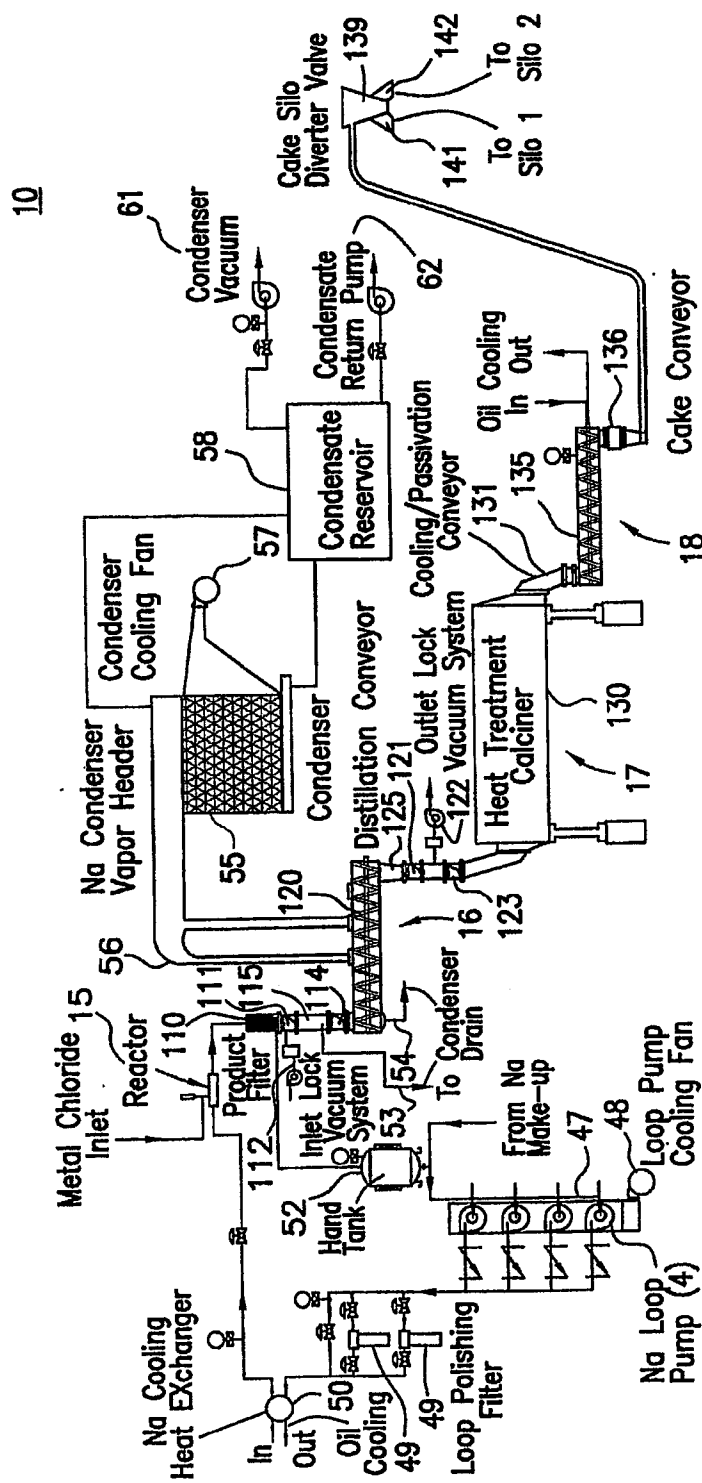


FIG. 3

4/4

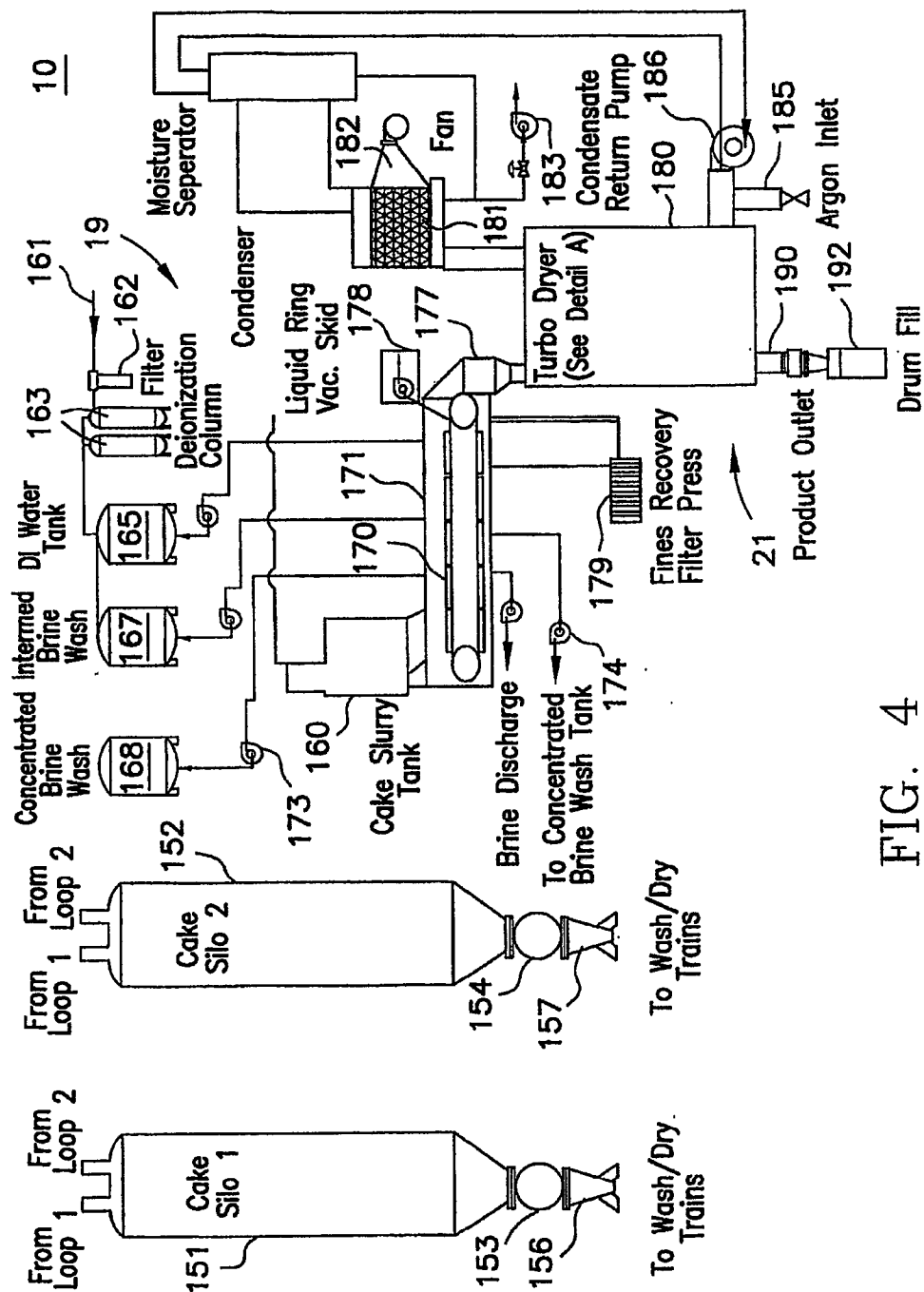


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/048828

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F9/28 C22B34/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/005090 A1 (ARMSTRONG DONN REYNOLDS [US] ET AL) 17 January 2002 (2002-01-17) paragraphs [0050], [0051]; claims	1-47
X	WO 2005/019485 A (INTERNAT TITANIUM POWDER LLC [US]; ERNST WILLIAM A [US]) 3 March 2005 (2005-03-03) claims	45-47

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

26 July 2007

Date of mailing of the international search report

06/08/2007

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

ALVAZZI DELFRATE, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2006/048828

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2002005090	A1	17-01-2002	NONE	
WO 2005019485	A	03-03-2005	NONE	